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Pt/MoO_x/MgO catalysts were prepared with varying Mo coverage and studied for the selective hydrodeoxygenation (HDO) of dibenzofuran (DBF) to biphenyl (BP), aiming at the elucidation of active sites for HDO. The oxophilic Mo species enrich the reducibility of surface Pt and the acidic sites of catalysts, change the product selectivity and then lead to significant improvement of the deoxygenation activity with an excellent HDO reaction rate (1.06 μ mol s⁻¹ g⁻¹) on Pt/7MoO_x/MgO compared with that (0.04 μ mol s⁻¹ g⁻¹) on Pt/MgO. Moreover, the catalytic performance can be controlled by MoO_x surface density and varied with the increased MoO_x surface density in a volcano-shape manner, in which at low Mo coverage (< 2.27 Mo/nm²), the dispersed Mo species are dominant that attribute to the active sites, and at further higher Mo coverage (> 6.19 Mo/nm²), the crystalline MoO₃ particulates may form that is detrimental to the activity. The highest BP yield (100 %) was obtained with Pt/7MoO_x/MgO close to monolayer of Mo coverage. Furthermore, reactivity studies in combination with density functional theory (DFT) calculations for the adsorption of dibenzofuran and H₂ indicate the synergy of Pt species in affording hydrogen species and adjacent MoO_x species in adsorbing/activating C-O bond suitable for the HDO of DBF.

1. Introduction

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Increasing environmental and economic awareness has aroused significant interest in the renewable production of liquid fuels and chemicals using lignin as a sustainable carbon source to replace fossil-derived resources¹⁻². However, the high content of oxygen-containing compounds³ leads to some drawbacks of fuels, such as low heating value, high viscosity, and poor thermal stability⁴. Catalytic hydrodeoxygenation (HDO) is an effective way to convert lignin into aromatic compounds⁵. Addressing the difficulty of sustainable production of aromatic compounds will need highly efficient catalysts with excellent selectivity.

The elementary reaction steps for HDO reactions mainly include the hydrogen dissociation and C-O activation⁶⁻⁸, which generally cannot be effectively activated by an active site⁶. Therefore, the most commonly HDO mechanism includes an active site that can activate hydrogen and another adjacent site capable of the effective activation of C-O bond. This suggests that diverse deoxygenation reaction can be best accomplished using bifunctional catalysts, in which two different active metals provide hydrogenation sites and adsorption sites of C-O bond that generate stronger metal-oxygen bonds⁶ respectively. This has prompted people to study the role of bimetallic catalysts containing a hydrogenating metal and an oxophilic metal⁹. The oxophilic metal may strongly anchor the molecules to the surface through their oxygen functional group, which makes the cleavage of C-O bond and alters reaction pathways¹⁰.

Extensive studies have aroused much interest in the reaction mechanism of bimetallic catalysts involving less-expensive and oxophilic Fe^{8, 11-12}, Mo¹³⁻¹⁶, or W^{7, 17-18} as a promoter to hydrogenating metal (such as noble metals) for deoxygenation applications. Vohs et al. proposed⁷ that the addition of WO_x to Pt/C promotes the cleavage of the C-O bond in m-cresol, in which the interaction between Pt and WO_x accelerates oxygen vacancy formation on the WO_x that promotes the hydrogenolysis of C-O bond, and adsorption on these sites also suppresses interaction between aromatic rings and Pt surface and then precludes the hydrogenation of aromatic rings. In hydrogenolysis of glycerol to 1,3-propanediol, the superiority of Pt-WO_x/ZrO₂ catalyst is attributed to the better synergy between Pt particles in affording the availabilities of hydrogen atoms and more Brønsted acidic sites for C-O scission¹⁹. The synergistic catalysis between Pd and Fe was also observed, in which Pd assists H₂ dissociation²⁰ and the reduced FeO_x promoted by Pd facilitates the adsorption/activation of C-O bond⁸. Further, Lee et al. also reported¹⁸ that the WO_x could improve the activity of Pd/Al₂O₃ in the HDO of guaiacol, especially, when the tungstate formed a near-perfect monolayer (3-5 W/nm²) on the support, which is related to the highest surface acidity for deoxygenation. However, at higher WO_x surface density, the formation of WO₃ crystallites leads to WO_x species being inaccessible to reactants²¹. Other researchers also found that the highest activity at monolayer of W coverage²². In detail, Xie et al. introduced the monolayer

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dispersion capacities for MoO₃ on various supports²³. As for the molecular structure of MoO_x on support²⁴, the isolated and oligomeric MoO_x exist on the support at low surface coverage, whereas the crystalline MoO₃ form above monolayer surface coverage (> 4.6 Mo/nm²)²³. The literature¹⁴ suggested that the modification of Mo to Pt/TiO₂ may facilitate the formation of more active hydrogen species from metal sites or metal-support interface, and thus improve the effective conversion of guaiacol. Richard et al.²⁵ further pointed out that the oxygen vacancies from MoO_x act as HDO active sites that could adsorb the oxygen atom of the phenolic reactant, which is consistent with the results by Infantes-Molina who proposed Mo species was capable of breaking C-O bond²⁶. DFT calculations suggested that the addition of Mo to the Pt surface could decrease aromatic-surface interaction that relates to increasing selectivity of C-O bond scission¹³. The interaction between Pt and Mo could also help to maintain the Pt in a highly dispersed form²⁷. Moreover, MoO_x can trap hydrogen with the formation of molybdenum oxide hydroxide²⁸ that may result in the formation of Brønsted acidic sites, which also provides a chance for hydrogen spillover²⁹. However, to the best of our knowledge, the mechanism of HDO reactions on supported Pt-MoO_x catalyst, including synergistic catalysis and effect of varying Mo coverage, has not been systematically studied and not well understood yet.

In the present study, dibenzofuran (DBF) was used as probe molecule for deoxygenation upgrading reactions since the C-O bond in this molecule is very difficult to break³⁰⁻³¹. We examined the activity of Pt/MoO_x/MgO catalysts with varying Mo coverage for HDO of DBF. A significant improvement in HDO activity was observed and biphenyl was major product with the addition of Mo. We further used the combined characterization of UV-vis, Raman, CO-IR, H₂-TPR, XPS, NH₃-TPD and TEM, to investigate the influences of the varying Mo coverage, the Pt-MoO_x interaction and the acidic properties of catalysts, on the HDO activity of the Pt/MoO_x/MgO catalysts. In particular, DFT calculations further confirmed the synergistic catalytic sites, which are responsible for the enhanced catalytic performance.

2. Experimental

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2.1. Preparation of catalysts

Pure MgO was prepared by hydrothermal precipitation. Typically, 25 mmol of $Mg(NO_3)_2$ was added to 50 ml of deionized water. Subsequently, urea was dissolved in aqueous solution with the molar ratio of urea and Mg (5:1). Then, the obtained solution was hydrothermally treated at 120 °C for 24 h. The precipitates were obtained by filtration and the impurities were removed by washing with deionized water and ethanol repeatedly. Then the samples were dried at 80 °C for 12 h and finally calcined at 500 °C (heating rate of 5 °C min⁻¹) for 4 h under O_2/Ar (20/40 mL min⁻¹) flow.

 MoO_x/MgO samples were obtained by impregnation with aqueous solutions containing a certain amount of $(NH_4)_6Mo_7O_{24}$ in order to obtain supports with different Mo contents (1, 3, 7, 10 wt.%). The obtained samples were dried at 120 °C for 12 h,

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and then calcined at 500 °C (heating rate of 5 °C min $\frac{1}{4}$ for the under O₂/Ar (20/40 mL min⁻¹) flow. The supports were defined as nMoO_x/MgO, in which n is the weight percentage of Mo (n = 0, 1, 3, 7, 10).

In all cases the catalysts were prepared by successive wetness impregnation method of methanol solution containing a certain amount of H_2PtCl_6 · GH_2O required to get a final metal loading of 3.0 wt.%. The samples were dried at 80 °C for 12 h and then calcined at 400 °C (heating rate of 5 °C min⁻¹) for 2 h under O₂/Ar (20/40 mL min⁻¹) flow. The obtained catalysts are denoted as Pt/nMoO_x/MgO (n = 0, 1, 3, 7, 10).

2.2. Characterization of catalysts

 N_2 physisorption isotherms were recorded on a Quantachrome Autosorb IQ instrument. Prior to the measurement, the samples were degassed under at 200 °C for 8 h in vacuum. The nitrogen adsorption isotherms were used to calculate the BET surface area at relative pressure of 0.05-0.3, average pore width using Density Functional Theory (DFT) method³², pore volume at relative pressure of 0.95.

Raman spectra were studied on a Thermo Scientific DXR Raman Microscope (Renishaw England). The line at 532 nm Ar laser served as excitation source and the scanning range was 50- 3500 nm^{-1} .

UV-vis spectra of samples were collected in the range from 200 to 800 nm on a UV-550 spectrometer (JASCO) using BaSO₄ as reference. The spectrum of MoO₃ was also measured as reference. The recorded reflectance (R_{∞}) was transformed to absorbance using the Kubelka-Munk function (F(R_{∞})) according to Equation (1). The absorption-edge energy was obtained by low energy rise of spectra using the intercept of the x-axis of the fitting line, [F(R_{∞})hv]² plotted as a function of hv, where hv is the energy of an incident photon, as previously reported²¹.

$$F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}}$$
 (1)

The X-ray diffraction (XRD) was carried out on a Rigaku D/MAX-RB instrument, using a Cu K α monochromatized radiation source. The patterns were recorded at a scan speed of 10° min⁻¹, between 2 θ range of 5°-90°, operated at 100 mA and 40 kV. The identification of phases was based on the standard cards.

The acidic property of the samples was determined by temperature programmed desorption (TPD) of ammonia on a CHEMBET-3000 chemisorption instrument. The sample (ca. 0.10 g) was reduced in a stream of H₂ by increasing linearly the temperature (10 °C min⁻¹) up to 400 °C holding for 2 h with 40 mL min⁻¹ flow. After cooling to 120 °C with He, the sample was subjected to a 10 % NH₃/He gas for 1 h. Then the gas was changed into He flow at 120 °C for 1 h in order to remove the physically adsorbed NH₃. Finally, the TPD experiment was run by increasing the temperature to 500 °C with a heating rate of 10 °C min⁻¹ under a 20 mL min⁻¹ flow of He.

Temperature programmed reduction (TPR) of the catalysts were determined on AutoChem II 2920 Chemisorption Analyzer. Before the measurements, the catalyst (~50 mg) was dried in an isothermal zone of a quartz U-tube reactor for 2 h at 300 °C in an He flow to remove the physically adsorbed water.

When the catalyst was cooled to ambient temperature, the TPR patterns were collected using a 10 % H_2 /He flow (30 mL min⁻¹) and the temperature was linearly increased to 800 °C at a heating ramp of 5 °C min⁻¹.

Transmission electron microscopy (TEM) was used to observe the particles of catalysts on a Tecnai G2 F30 (FEI) instrument, operating at 300 kV accelerating voltage and equipped with an EDX system for measuring X-ray energy dispersive spectra. Before TEM analysis, the catalysts were reduced in the same conditions as reaction experiment. Scanning electron microscopy (SEM) pictures of the samples were collected on a FEI Nova Nano SEM 450 electron microscope with a voltage in the range of 0.5-30 kV.

The samples were studied by the infrared spectra of adsorbed CO to explore the effect of Mo addition on the Pt species. The spectra were recorded on a Bruker Equinox 55 spectrometer equipped with a DTGS detector, at a resolution of 4 cm⁻¹ using coaddition of 500 scans. Before the adsorption, the already reduced samples were pre-treated in flowing 10 % H₂/Ar at 300 °C for 1 h. Afterwards, the samples were cooled down to ambient temperature and then subjected to flowing He for 30 min, followed by adsorption of 10 % CO/He flow (20 mL min⁻¹). Then, the gas phase CO was completely removed with molecular pump when the spectra were unchanged.

X-ray photoelectron spectroscopy (XPS) was recorded using a photoelectron spectrometer (ESCALAB250) equipped with a monochromatic Al Ka X-ray source (1486.6 eV), operated at 15 kV and 20 mA. The catalysts were reduced at ex-situ condition (400 °C for 2 h under 40 mL min⁻¹ H₂ flow) and then put in a rigorous vacuum generally in the order of less than 3.5×10^{-7} Pa. The adventitious carbon (C 1s) peak at 284.6 eV was regarded as internal reference. The chemical state was estimated by the areas of the peaks from curve fitting the Mo 3d, Pt 4f regions using the XPSPEAK software.

The CO pulse adsorption was performed on AutoChem II 2920 Chemisorption Analyzer. Prior to measurement, the samples were reduced under H_2 flow at 400 °C for 2 h, and the adsorption of 10 % CO/He was performed at 30 °C. CO adsorption was accomplished under the same three successive peak areas. The adsorption stoichiometry between CO and active sites was assumed to be 1:1.

2.3. Catalytic reaction

Catalytic performances were performed in a vapor-phase fixedbed reactor, as described elsewhere³³. Generally, the hydrodeoxygenation of DBF was carried out at 400 °C and 0.1 MPa. The catalyst (0.08 g) was mixed with 60-80 mesh SiO₂ (5.0 mL) and kept in the middle of two inert layers of SiO₂. Before the experiments, the catalyst was reduced in the reactor at 400 °C for 2 h under a H₂ flow rate of 40 mL min⁻¹. After that, DBF was delivered into the reactor via a pump. Catalytic activities were measured after the reaction was run overnight to keep reaching the steady state. The liquid reactants were made up of 2.0 wt.% DBF, 97.0 wt.% n-decane (as solvent) and 1.0 wt.% *n*dodecane (as internal standard). The liquid products were quantified in a Agilent chromatograph (7890A, 0.5 μ m × 0.32 mm × 30 m FFAP). The carbon balance has been checked to ensure that more than 95 % was reached for each experiment. Flow rates were adjusted to obtain different contact time 4(f) values.

$$\tau = W/F$$
 (2)

where W is the catalyst weight (g) and F is the weight flow rate of the reactant (g min⁻¹).

The conversion (X) of DBF, the selectivity (S_i) of products and degree of hydrodeoxygenation (HDO), were expressed as follows:

$$X = (n_0 - n_{DBF})/n_0 \times 100\%$$
(3)

$$S_i = n_i / \sum n_i \times 100\% \tag{4}$$

$$HDO = \sum n'_i / \sum n_i \times 100\%$$
 (5)

where n_0 and n_{DBF} denote the moles of DBF in the feed and product, respectively, n_i denotes the moles of i product molecule, $\sum n_i$ is the total moles of products and $\sum n_i'$ is the sum of moles of products that do not contain oxygen.

The rate constant (k, min⁻¹) of reaction can be calculated at low conversion, assuming that the reaction is a first-order reaction, according to the following equation:

$$\mathbf{k} = -\frac{F}{W}\ln\left(1 - X\right) \tag{6}$$

The specific reaction rate (r, μ mol·s⁻¹·g_{cat}⁻¹) can be calculated as follows³⁴:

$$r = kC_0 = -\frac{w_{DBF}F}{M_{DBF}W} \ln(1-X)$$
 (7)

where C_0 represents the initial concentration of DBF (mol g⁻¹), w_{DBF} represents the weight fraction of DBF in the reactant and M_{DBF} is the molecular mass of DBF.

The intrinsic reaction rate TOF (s⁻¹) is expressed by

$$TOF = \frac{r}{n} * N \tag{8}$$

with n is number of active sites (according to CO chemisorption) and N is Avogadro Number.

2.4. Density functional theory calculations

Spin polarized density functional theory (DFT) calculations³⁵⁻³⁶ were carried out with the Perdew-Burke-Ernzerhof (PBE) exchangecorrelation functional as implemented in the Quantum ESPRESSO program package³⁷. A plane wave basis set with an energy cutoff of 48 Ry (~ 407 eV) was employed for the wavefunction, whereas that for the charge density was set to 350 Ry. The geometry was optimized using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme until the convergence of the total energy reaches 10^{-4} Ry and that of the atomic force is below 10^{-3} Ry/Bohr (~ 0.03 eV/Å). "gaussian" smearing with a width of 0.005 Ry (~ 0.07 eV) was used to assist the energy convergence. A Monkhorst-Pack k-point mesh of (6×6×1) was employed for the MoO₂ (011), MoO₃ (010) and Pt (100) slab models.

Supported MoO₂, MoO₃ and Pt nanoparticle catalysts were modeled with MoO₂ (011), MoO₃ (010) and Pt (100) slab models, respectively, as showed in Fig. 1. The slab model of MoO₂ (011) was built from the optimized monoclinic bulk MoO₂ unit cell with the cell parameters a = 5.584, b = 4.842, c = 5.608, β = 120°. It consists of 48 Mo and 80 O atoms, resulting in a supercell dimension of 14.67 Å×11.17 Å×25.74 Å. The slab model of MoO₃ (010) was built from the

optimized orthorhombic bulk MoO₃ unit cell with the cell parameters a = 3.9624, b = 13.860, c = 3.6971. It consists of 36 Mo and 90 O atoms, resulting in a supercell dimension of 11.09 Å×11.89 Å×25.74Å. The slab model of Pt (100) was built from the optimized face-centered-cubic (fcc) bulk Pt unit cell with the cell parameters a = b = c = 3.89 Å, and it consists of 98 Pt atoms distributed in four atomic layers with an interlayer spacing of 20 Å, resulting in a supercell dimension of 11.67 Å × 11.67 Å × 25.83 Å.

Atoms in the bottom two layers of slab models were frozen at their bulk equilibrium positions, whereas those in the top two layers as well as the organic or hydrogen adsorbates were allowed to relax for MoO_2 (011) and Pt (100). For MoO_3 (010) slab model, Atoms in the bottom three layers were frozen at their bulk equilibrium positions, whereas those in the top three layers as well as the organic or hydrogen adsorbates were allowed to relax.

The adsorption energy (ΔE_{a}) of an adsorbate A over a catalyst C is defined as:

$$\Delta E_a = E_{A/C} - E_A - E_C$$
(9)

where E_A is the total energy of the isolated adsorbate, and $E_{A/C}$ and E_C are the total energies of the catalyst with and without the adsorbate. More generally, relative energies on the potential energy surface are calculated using the isolated molecular reactants and the pristine slab model as the reference.



Fig. 1. Side view of the MoO_2 (011) slab model (a); MoO_3 (010) slab model (b) and Pt (100) slab model (c). Mo, O, Pt atoms are show in light blue, red, cyan, respectively.

3. Results

3.1. Catalyst structure after Mo-incorporation

The textural properties of samples are presented in Table 1. The addition of Pt and Mo to the MgO resulted in the decrease of the surface area and pore volume to variable degrees. However, the pore size resulted in a significant increase, consistent with our previous result³³. These results suggest that

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the addition of Pt and Mo has a significant influence anothe structure of MgO. Interestingly, compared With 3the catalysts with small Mo loading (1 and 3 wt.%), Pt/MgO suffered a considerable decrease in surface area as well as pore volume, which seems to indicate that the addition of Mo could stabilize the structure of MgO. The Pt content of catalysts is in agreement with the theoretical value (3 wt.%), and as is expected, an increase in Mo loading observed.

Powder XRD diffraction patterns obtained for Pt/MoO_x/MgO samples are presented in Fig. S1. All the catalysts present the characteristic peaks of the MgO structure. No peaks of platinum and molybdenum oxide was observed, even for the highest loading of 10 wt.% Mo, which indicates that the Pt and Mo particle might be small enough to fall below the detection limit. Besides, the results show the intensity of the MgO signals gradually reduced along with the increase of Mo loading. This can be related to the decreasing proportion of MgO in the sample and/or to an actual reduction of the crystallinity of the MgO structure due to the Mo addition³⁸.

UV-vis DRS spectra were used to explore the local structure of MoO_x on the MgO supports, focusing on ligand-to-metal charge transfer (LMCT) transitions (Figs. 2 and S2) and their corresponding absorption-edge energies (E_g) (Table 2). UV-vis spectrum of MgO exhibited only one strong LMCT absorption band at ~ 220 nm and the band shifted to higher wavelength with the addition of Mo species (Fig. S2), which is indicative of the interaction between MgO and MoO_x. The UV-vis E_g values (Table 2), calculated from Fig. 2, reflected the degree of oligomerization of molybdates and they were decreased with the increase of the number of Mo-O-Mo bonds³⁹. The lower E_g value was characteristic of oligomeric molybdates^{24, 39}. The absorption-edge energies of samples shifted to lower values with the addition of Mo.

The E_g values of the MoO_x on supported-catalysts linearly decreased from 3.63 to 3.35 eV with the increase of Mo coverage, indicating an increase of Mo-O-Mo bonds is related to the MoO_x oligomers²⁴. The number of Mo-O-Mo bonds for the supported MoO_x could be calculated from the E_g vs Mo-O-Mo relationship based on previous report³⁹. The phase of the MoO_x could transform based on its surface coverage^{18, 40-41}. At low Mo coverage (< 2.27 Mo/nm²), the polymolybdate are major species. On further increased Mo coverage (> 6.19 Mo/nm²), the crystalline MoO₃ may form on top of the polymolybdate layer, which is strongly affected by the number of Mo-O-Mo bond according to literature^{21, 39}. Moreover, it had

Samples	S ^a	Va	d ^a	Pt loading	Mo loading	(Mo/Pt)	Mo (nm ⁻²)	CO uptake	Dispersion
	(m²/g)	(cm³/g)	(nm)	(wt.%)	(wt.%)	atomic ratio		(µmol/g)	(%)
MgO	148	0.25	3.6	-	-	-	-	-	-
Pt/MgO	77	0.24	7.5	2.94	-	-	-	14.56	10
Pt/1MoO _x /MgO	107	0.49	11.2	3.34	0.88	0.54	0.52	22.77	13
Pt/3MoO _x /MgO	96	0.46	8.5	2.85	3.48	2.48	2.27	22.52	15
Pt/7MoO _x /MgO	77	0.38	7.5	3.33	7.60	4.64	6.19	23.79	14
Pt/10MoO _x /MgO	71	0.39	7.5	3.12	10.07	6.55	8.90	20.77	13

^a BET surface area (S), total pore volume (V), and average pore width (d) as determined by N₂ adsorption-desorption isotherms at -196 °C

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been observed that Mo species absorbing strongly on supports resulted in the decreased absorption-edge energies⁴², thus the decreased absorption-edge energies with increasing Mo addition indicate a higher interaction between Mo species and MgO. The reduction process cannot significantly influence the structure of MoO_x based on the similar absorption-edge energies of supports at different oxidation and reduction states.



Fig. 2 $[F(R_{\infty})hv]^2$ as a function of energy (hv) for the MoO_x/MgO supports at oxidation states (a) and reduction states (b) at 400 °C for 2 h under H₂ flow, from UV-vis DRS spectra.

Table 2	Absorption-edge	energy of MoO	/MgO determined	from UV-vis	spectroscopy
			······································		

Samples	Absorption-edge energy of support at oxidation states (eV)	Absorption-edge energy of support at reduction states (eV)
MgO	5.17	5.17
1MoO _x /MgO	3.63	3.60
3MoO _x /MgO	3.53	3.55
7MoO _x /MgO	3.45	3.47
10MoO _x /MgO	3.35	3.23
MoO ₃	3.13	-

Raman spectroscopy was carried out to probe the nature and structural information of the supported metal oxides (Fig. 3). The band at 1093 cm⁻¹ originated from the magnesia support. At higher loadings a surface polymolybdate species was observed which exhibits strong characteristic peaks in the stretching region of Mo=O at ~ 917 cm⁻¹ and of Mo-O-Mo at 806 and 213 cm⁻¹.^{24, 41} The relative concentration of isolated and polymeric molybdate species on magnesia support increased as the surface Mo coverage increased. The strong peak at 870 cm⁻ ¹ was related to Mo-O-Mg stretch. The band at ~ 325 cm⁻¹ was assigned accordingly to the asymmetric MoO_4 bending mode³⁹. For the 7 wt.% MoO_x/MgO (6.19 Mo/nm²) catalysts, MoO₃ crystallites together with molybdate species were present on the magnesia surface, as reflected by the appearance of the bands at ~ 917, ~ 870, ~ 806, and ~ 200-400 $\rm cm^{-1}$, indicating that the monolayer coverage of MoO_x has been reached³⁹. For the further 10 wt.% MoOx/MgO (8.90 Mo/nm²) catalyst, the position of Mo=O vibration shifted to ~ 917 cm⁻¹ and a new band appeared at ~ 213 cm⁻¹ which can be associated with Mo-O-Mo vibrations, suggesting oligomerization of some surface molybdate species and the presence of MoO₃ crystallites, as also detected by UV-vis. These indicate that pseudo monolayer coverage of the molybdate species has been reached for a value of Mo surface density between 2.27 and 6.19 Mo/nm². The similar result was also seen in MoO_3/CeO_2^{43} and WO_3/ZrO_2 catalysts44.



Fig. 3 Raman spectra of calcined nMoO_x/MgO (n = 0, 1, 3, 7, 10) supports.

3.2. Electronic property of catalysts

IR spectroscopy of CO adsorbed on three catalysts was used to characterize the electronic states of Pt species (Figs. 4 and 5). The two bands at 2172 and 2120 cm⁻¹ were attributed to CO adsorption on the Mg²⁺ cation³⁰ as shown in Fig. 4. As the number of O²⁻ anions (n) coordinated to Mg²⁺ decreased, the position of CO shifted to higher wavenumbers ($u_{n=4} = 2120 \text{ cm}^{-1}$, $v_{n=3} = 2172 \text{ cm}^{-1})^{45}$. Additionally, two main bands appeared in the spectra⁴⁶: a strong band observed in 1950-2100 cm⁻¹ region, where several overlapping bands with local peaks and shoulders belong to a linear CO (L) with the combination of CO attached to highly coordinated Pt atoms (2068 cm⁻¹) such as terraces, and CO adsorbed on low coordinated Pt sites (2020 cm⁻¹) at stepedges, corners or defects⁴⁷, and another broad signal at about 1811 cm⁻¹ that belongs to bridged CO (B)¹² (Fig. 4). The peaks of CO adsorption on Pt sites were easier to saturate than that on the Mg²⁺ cation (Fig. 4), indicating the stronger interaction between CO and Pt sites, as can also be observed by the disappearance of the bands with the removal of the gas phase CO (Fig. 5).



Fig. 4 FTIR spectra of step-wise CO adsorption on (a) $7MOO_x/MgO$, (b) Pt/MgO and (c) Pt/ $7MOO_x/MgO$ after in-situ reduction in flowing H₂.

It is noteworthy that the addition of Mo led to an increase of peak intensity at 2020 cm⁻¹ that is attributed to low coordinated Pt sites. The intensity ratio of bridged to linear (B/L) bonded CO was increased from 0.20 to 0.32 with the addition of Mo. The change of the band position and the values of B/L testified that

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electron transfer from Mo to Pt occurred and then the electron density of Pt increased, which was induced as a result of proximity between Pt and Mo. This electronic modification of Pt was in line with previous results reported by our group³⁰. Similar phenomenon has also been found for the Pt-Fe/SiO₂ by CO-IR and XANES, and such a shift is related to the increasing electron



density of Pt species¹², which in turn increases the extent of the

back donation to the CO $2\pi^*$ orbitals⁴⁸.

Fig. 5 IR spectra of CO adsorbed on 7MoO_x/MgO, Pt/MgO and Pt/7MoO_x/MgO after the removal of the gas phase CO.

The electronic interactions and chemical states of catalysts were revealed by XPS as shown in Fig. 6. In Pt/1MoOx/MgO sample, the Mo 3d spectrum was quite noisy and therefore difficult to be assigned. The dispersed MoO_x was difficult to be reduced below monolayer coverage of Mo, whereas once the coverage of the monolayer was exceeded, MoO₃ crystallites were formed, which can undergo facile reduction to less reactive MoO_2 (Table 3). Besides, the surface Pt^0 species gradually increased with the addition of Mo until the Mo coverage reached 6.19 Mo/nm². It demonstrates an intensive electron transfer from Mo species to Pt with the modification of MoO_{x} , thus ensuring close contact between the Pt and MoO_{x} . The surface Mo/Pt atomic ratio increased almost linearly with the Mo surface densities of the Pt/MoO_x/MgO catalysts (Table 3 and Fig. S4), indicating that Mo species were homogeneously dispersed over the surface of catalysts.



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Samples		Distribution of valence states (%)						
	P	't		Мо				
	Pt ⁰	Pt ²⁺	Mo ⁶⁺	Mo ⁵⁺	Mo ⁴⁺	ratio		
						(Mo/Pt)		
Pt/MgO	74.81	25.19	-	-	-	0		
Pt/1MoO _x /MgO	75.34	24.66	-	-	-	0.25		
Pt/3MoO _x /MgO	81.27	18.73	59.21	20.22	20.57	1.70		
Pt/7MoO _x /MgO	89.07	10.93	63.99	19.77	16.24	2.82		
Pt/10MoO _x /MgO	84.22	15.78	54.67	13.35	31.99	3.83		

3.3. Reducibility of catalysts

The impact of modification of Mo species on the reducibility of catalysts was explored by H₂-TPR (Fig. 7). The peaks in the range of 200-500 °C for the catalysts belonged to the reduction of Pt species. The peak of hydrogen consumption at maximal temperature (\sim 700 °C) for the catalysts with above 7 wt.% Mo (6.19 Mo/nm²) was assigned to the reduction of crystalline MoO₃, which was consistent with XPS results, as also can be confirmed by the H₂-TPR of bulk MoO₃ (Fig. S3). For Mo coverage below the monolayer value there would be a strong interaction between Mo species and MgO and thus the reducibility of MoO_x is more difficult, which is in agreement with the results of W supported on $Al_2O_3^{49}$. However, for the Mo coverage at above 7 wt.% Mo (6.19 Mo/nm²), the Mo species is significantly easy to be reduced, which indicates that MoO₃ crystallites are present on the magnesia surface²¹, and are in accord with the results of UV-vis and Raman spectra. Note that the main reduction temperature of Pt species decreased with the Mo coverage increased to 7 wt.% Mo (6.19 Mo/nm²), followed by an increase in higher Mo coverage. It may be due to the electron transfer from Mo species to Pt that leads to the further reduction of Pt, as is confirmed by CO-IR. With the higher Mo coverage (reached monolayer), the formation of crystalline MoO₃ species was detrimental to the reduction of Pt. Besides, the decrease in the hydrogen consumption in the range of 0-2.27 Mo/nm² may be responsible for an increase of electronic interaction between Pt and Mo via a partial decoration of Pt by MoO_x species and thus contribute to the appearance of electron-rich Pt^{18, 49}, an evidence of close contact between Pt and MoO_x species, which is similar to the Re-MoO_x/TiO₂ catalysts⁵.



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Fig. 8 Morphology and structure characterization of the Pt/7MoO,/MgO: (a) SEM of MgO; (b, c) HRTEM images; (d, e) HAADF-STEM image and corresponding STEM-mapping of Mg, O, Pt, and Mo; (f) STEM-EELS line scan.

3.4. Structure of samples revealed by SEM and TEM

SEM showed the synthetic MgO was sheet-like (Fig. 8a). A representative TEM image of Pt/7MoO_x/MgO (Fig. 8b) showed that the metallic particles were uniformly dispersed on the surface of MgO (average width ca. 1.78 nm). Nevertheless, no further conclusion on the size of individual Mo and Pt particles can be made due to indiscernible contrast between the MoO_v and Pt particles. HRTEM observations suggested the existence of separate MoO_x and Pt particles over MgO (Fig. 8c). The Pt exposed (111) plane has interlayer spacing of 0.227 nm. The STEM and STEM-mapping results (Figs. 8d and e) showed that MoO_x and Pt particles were uniformly and separately distributed in the tested region, especially with the higher magnitude image (Fig. 8e). The STEM-EELS line scan further confirmed that Mo and Pt were separate and may be not form an alloy (Fig. 8f).

3.5. Surface acidity of catalysts

Table 4. NH₃-TPD results of Pt/MoO_v/MgO catalysts reduced at 400 °C for 2 h.

Samples	Aci	Acidic site		
	Weak	Strong	Total	density (µmol NH₃/m²)
Pt/MgO	0.05	0.07	0.12	1.55
Pt/1MoO _x /MgO	0.08	0.07	0.15	1.39
Pt/3MoO _x /MgO	0.12	0.11	0.23	2.35
Pt/7MoO _x /MgO	0.15	0.12	0.27	3.54
Pt/10MoO _x /MgO	0.16	0.11	0.27	3.82

The amounts of acidic centers were estimated by NH₃-TPD of catalysts (Fig. 9), and the corresponding values are presented in Table 4. The total of acidity reached a maximum at Pt/7MoO_x/MgO with an increase in the Mo coverage, which featured a molybdate near-monolayer on catalyst surface in accordance with the results of UV-vis and Raman, and then stabilized as the Mo content exceeded 7 wt.%. These results

indicate that the dispersed molybdates are the main acidic sites¹⁸ whereas the molybdate crystallites have lesser acidity as also evidenced by NH₃-TPD of bulk MoO₃ (Fig. 9). The results are in agreement with other work⁵⁰.



Fig. 9 NH₃-TPD patterns of Pt/nMoO_x/MgO (n = 0, 1, 3, 7, 10) catalysts reduced at 400 °C for 2 h under H₂ flow.

3.6. Catalytic performance

In this work, the activity of Mo-promoted Pt catalysts were studied in the hydrogenolysis of dibenzofuran. For better investigation how the oxophilic Mo species affect the removal of oxygen atom in dibenzofuran, we select feasible reaction conditions (400 °C and 0.1 MPa) to yield just two products, ophenylphenol (OPP) and biphenyl (BP) as displayed in Fig. 10a. The major product was OPP on Pt/MgO with the highest relative concentration of 30 % at contact time of 1.8 min. Then the relative concentration of OPP decreased and the amount of BP exceeded that of OPP at the contact time of 2.7 min. It demonstrated that the catalytic transformation of DBF underwent the only one C-O bond scission to OPP, followed by the deoxygenation of OPP to BP.

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Fig. 10 (a) Relative concentration of the hydrogenolysis of DBF over Pt/MgO as a function of contact time, and (b) the BP selectivity over Pt/nMoO₂/MgO (n = 0, 1, 3, 7, 10) as a function of conversion.



Fig. 11 The conversion and TOF for Pt/MoO₂/MgO catalysts at varying Mo surface density (Mo/nm²) during the hydrogenolysis of DBF at 400 °C, 0.1 MPa and 0.84 min.

The selectivity at different conversion for the Pt/MoO_x/MgO catalysts is presented in Fig. 10b. As the DBF conversion increased, the selectivity toward BP over all the catalysts increased. Maximum BP selectivity of 100 % was obtained at 100 % conversion over Pt/7MoO_x/MgO, which suggests that Pt/7MoO_x/MgO was an excellent catalyst for the HDO of DBF with improved conversion and BP selectivity simultaneously. At fixed conversions (30 %), the BP selectivity enhanced dramatically from 20.5 % (Pt/MgO) to 61.8 % (Pt/1MoO_x/MgO) and then to about 95.7 % with the coverage of Mo at 7 wt.% (6.19 Mo/nm²), which indicates that small amounts of Mo could significantly increase the removal of oxygen atom. At the same contact time, the activity varied with the Mo coverage in a

volcano-shape manner, and the best catalyst is $Pt/7MoO_x/MgO$ (Fig. 11). The intrinsic reactivity on Mo coverage also followed the volcano-type dependency (Fig. 11), which was the same as the trend of conversion of DBF. The HDO of DBF study for a series of $Pt/MoO_x/MgO$ catalysts confirmed both deoxygenation rate and selectivity increased significantly with the increase of Mo coverage.

To elucidate the effect of Mo and Pt in the reaction process, intrinsic reactivity of catalysts was defined as the intrinsic reaction rate normalized by the molar of Mo and Pt species (Table 5). The initial reaction rates (r), estimated from the low conversion according to equation (7), were found to increase essentially with the Mo surface densities increased to 6.19 Mo/nm², whereas at higher Mo surface densities (8.90 Mo/nm²) a gradual decrease in the r was observed, which is consistent with the variation tendency⁵¹ of conversion and TOF (Fig. 11). Furthermore, for sub-monolayer coverages, the HDO rate (formation rate of BP) also increased as the Mo coverage reached to a close monolayer (6.19 Mo/nm²) and then followed by a decrease in activity with further Mo addition that resulted in the formation of MoO₃ crystallites, suggesting that dispersed Mo species is efficient in the acceleration of the deoxygenation process whereas MoO₃ crystallites have lower activity that may reduce the availability of reactive species for reactions⁵². Similarly, the reaction rate and HDO rate per Pt atom also demonstrated that the addition of Mo species within monolayer could promote the hydrogenolysis of DBF and especially the removal of oxygen atom¹³. In conclusion, these results indicate that the use of Pt/MoOx/MgO catalysts may lead to excellent

Table 5. Conversion of DBF and HDO rates expressed as specific (µmol s⁻¹ g⁻¹) and intrinsic (mmol s⁻¹ mol_{Pl}⁻¹, mmol s⁻¹ mol_{M0}⁻¹) rates for Pt/MoO_s/MgO catalysts.

Catalysts		r _{DBF}			r _{HDO}		TOF promotional
	µmol s-1 g-1	mmol s ⁻¹ mol _{Pt} ⁻¹	mmol s ⁻¹ mol _{Mo} ⁻¹	µmol s-1 g-1	mmol s ⁻¹ mol _{Pt} ⁻¹	mmol s ⁻¹ mol _{Mo} ⁻¹	factor
Pt/MgO	0.67	4.45	-	0.04	0.25	-	1
Pt/1MoO _x /MgO	1.06	6.15	11.48	0.28	1.65	3.08	1.09
Pt/3MoO _x /MgO	1.14	7.82	3.16	0.83	5.66	2.29	1.24
Pt/7MoO _x /MgO	1.31	7.65	1.65	1.06	6.22	1.34	1.33
Pt/10MoO _x /MgO	1.09	6.78	1.04	0.89	5.55	0.85	1.29

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Fig. 12 The catalytic behavior of Pt/7MoO_x/MgO, 7MoO_x/MgO and Pt/MgO: (a) The conversion of DBF as a function of contact time and (b) product selectivity at contact time of 1.2 min.

deoxygenation activity, which are unfavorable on monometallic Pt catalysts⁶.

To further explore the effect of Pt and MoO_x on the catalytic reaction, the conversion and selectivity on the Pt/7MoO_x/MgO, 7MoO_x/MgO and Pt/MgO catalysts were compared as shown in Fig. 12. The results showed that the Pt/MgO catalyst exhibited relatively poor activity and BP selectivity compared with Pt/7MoO_x/MgO, suggesting that although Mo itself showed no catalytic activity (Fig. 12a), it plays an important role in the addition of Mo to Pt/MgO. Therefore, the Mo addition enhanced the activity and HDO capability of catalyst that exists variant catalytic active sites in comparison with the monometallic ones.

The Pt/7MoO_x/MgO catalyst was more active than monometallic ones, thus indicating that the high activity of Pt/MoO_x/MgO must be due to synergistic interactions between the Pt and MoO_x^{16} , in which the presence of MoO_x species improves the activation of C-O bond of DBF and the Pt species are responsible for hydrogen activation and donation⁵. It is noteworthy that 7MoO_x/MgO catalyst was completely inactive. And it can be explained as follow, although the O-group of DBF could be strongly adsorbed on the 7MoO_x/MgO surface by the interaction between Mo and O, the absence of dissociated H on the metallic sites contributed to the low activity for the reaction. On the other hand, although 7MoO_x/MgO catalyst was considerably less active than Pt/MgO, the high BP selectivity over 7MoO_x/MgO far exceeded that over Pt/MgO (Fig. 12b), which seems to indicate that the adsorption of oxygencontaining species mainly takes place on MoO_v species surface. The similar results⁷ have also been found in the hydrogenolysis of m-cresol on Pt-WO_x/C catalysts, in which the HDO reaction occurs by a direct cleavage of C-O bond adsorbed on oxygen vacancy (or redox) sites on WO_x species.

4. Discussion

4.1. Identification of the catalytic active sites of Pt/MoO_x/MgO catalysts

To discuss the feasible sources of the high activity and selectivity of $Pt/MoO_x/MgO$ catalysts for the deoxygenation of DBF to form BP, the catalytic performance of Pt/MgO with different Mo content was compared. Our results show that the addition of Mo could evidently increase the BP selectivity as well as activity of catalyst, and the explanation for this can be mainly related to the fact that differences in the surfaces properties of the catalysts contribute to the variations in activity and selectivity.



Fig. 13 Adsorption configurations of dibenzofuran on (a) MoO₂ (011), (b) MoO₃ (010 and (c) Pt (100) surfaces, respectively.

Table 6. Adsorption energies for H (ΔE_{a1}) and dibenzofuran (ΔE_{a2}) on MoO ₂ (011), MoO
(010) and Pt (100) surfaces respectively

Surface	ΔE_{a1}	ΔE_{a2}
MoO ₂ (011)	-1.10	-1.04
MoO ₃ (010)	-3.52	-4.30
Pt (100)	-0.43	-0.29

To determine the active sites for the catalytic hydrogenolysis of dibenzofuran on catalyst surface, the adsorption of dibenzofuran and hydrogen on MoO_2 (011), MoO_3 (010) and Pt (100) was studied using DFT, as shown in Figs. 13 and S5. The most stable configuration of dibenzofuran adsorption was found to be in flat configuration with an angle. The resulting adsorption energies of dibenzofuran and hydrogen are shown in Table 6. MoO_3 had a stronger adsorption strength of dibenzofuran than MoO_2 and Pt, suggesting that dibenzofuran adsorption is more favorable on the oxophilic Mo sites, especially for MoO_3 . Besides, Pt absorbed hydrogen more easier than dibenzofuran. The cleavage of C-O bond was often not

favored on noble metals like Pt that may not strongly bind oxygen, even when the energy of C-O bond is relatively weak⁶. The H₂-TPD (Fig. S6) also indicated that Pt was more likely to adsorb H₂, whereas MoO_x almost had no adsorption peak of H₂. These results show that Mo sites are for the adsorption of dibenzofuran and Pt sites are for the activation of H₂. Thus, the cleavage of C-O bond may be easier on oxophilic Mo sites adjacent Pt sites, leading to higher HDO reactivity.

The explanation for the improved activity can be mainly due to the fact that MoO_x as the oxophilic species facilitates the adsorption of C-O bond and then results in the C-O bond weakening and breaking⁵¹ as can be confirmed by improved acidic sites (Fig. 9) and DFT calculation (Table 6). The coordinatively unsaturated sites of Mo cation promote the adsorption of DBF and then activate C-O bond, thus increase the activity of catalyst as well as selectivity to deoxygenation^{5, 53}. The enhanced activity is considered to be due to strong Mo-O interactions that allowed a phenoxy species of the DBF to form strong tethering to the surface. The surface phenoxy formed by this C-O scission can either undergo hydrogenolysis to produce OPP as a primary product or further cleave the C-OH bond to produce the phenyl that leads finally to BP. The former dominates on Pt/MgO and OPP is the primary product, but the latter is definitely dominant on Mo, which explains why few OPP is observed over Pt/MoO_x/MgO catalyst. The understanding how the oxophilic metal affects the selectivity of deoxygenation were similar as Pt/Fe_2O_3 catalyst for the hydrogenation of anisole¹⁰. DFT calculations also indicate that the Mo sites are contributed to the adsorption of dibenzofuran and then significantly improve the deoxygenation activity.

It is noteworthy that the amounts of acidic sites of catalysts regularly changed in volcano-type with the MoO_x addition, in agreement with the volcano-type activities. The UV-vis and Raman, together with NH_3 -TPD, indicated that the dispersed molybdate was the main acidic sites^{18, 54} whereas the molybdate crystallites had lesser acidity. The discrepancy in bond energy of metal-oxygen may be related to the ability to form unsaturated vacancies which can act as acidic sites^{5, 55}. The

partially-reduced metallic oxide could contribute to the acidity of the catalysts^{5, 46}. These may be the 19easer own 23the introducing Mo species to Pt/MgO facilitated new creation of acidic sites. The addition of Mo species with higher acidity improves the selectivity to deoxygenation, which is associated with its capacity to the C-O bond scission^{26, 56}. This phenomenon was observed for the hydrogenolysis of tetrahydrofurfuryl alcohol on Rh-MoO_x/SiO₂, with enhanced C-O bond scission resulted from the formation of the partially reduced isolated MoO_x species⁵⁷. Previously, the introduction of oxophilic W to Pt/t-ZrO₂ also increased the acidic sites of catalysts and contributed to the activation of the hydroxyl group, thus increased the transformation of glycerol^{17, 19}. Therefore, the generation of acidity may be the embodiment of oxophilicity of Mo species.

The electronic modification of the catalytic sites also plays an important role in the increased activity of catalysts. The electronic effect can arise from the interaction between Pt and Mo species. CO-IR and XPS reveal a higher fraction of electronrich Pt by electron transfer from Mo to Pt and a lower oxidation state of Pt⁵⁸, consistent with the results of H₂-TPR and XPS, in which a certain amount of Mo increased the reducibility of Pt supported on magnesia. Furthermore, DFT and H₂-TPD suggest that active Pt contributes to the activation/dissociation of hydrogen and thus results in more active H-species that could participate in the reaction. On the other hand, oxophilic Mo site hypothetically has changed electronic properties and is in a coordination unsaturated state due to enhanced hydrogen activation by Pt, as confirmed by XPS (Fig. 6), which is the active site for the C-O bond scission. Notably, Mo sites on the Pt-Mo catalysts may be reduced by the spillover effect, in which Pt is responsible for activation of H₂ that could migrate to Mo sites⁵⁹. This hydrogen spillover has also been found in previous work with Pt-Mo²⁸, and can be promoted by acidic sites of the support⁶⁰, which is in accordance with the amount of acidic sites. It may lead to the conclusion that dibenzofuran prefers to adsorb on the Pt-modified Mo sites.



Fig. 14 Hydrodeoxygenation (HDO) reaction rate with Mo surface density (Mo/nm²) for Pt/MoO_x/MgO catalysts (a) at the contact time of 0.15 min and corresponding proposed reaction mechanism (b).

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In Pt/MoO_x/MgO, there is a significant interaction between Pt and Mo species. The addition of Mo species reduces the interaction between Pt and MgO and then weakens the reduction temperature of Pt species. In this respect, the more active Pt sites may emerge and thus produce more dissociated H species. It proves that the ability of dissociated H species on Pt sites enhances with the addition of Mo species. We have also used TEM to show the close contact between MoO_x species and Pt species. The Pt/7MoO_x/MgO catalyst was more active than its monometallic ones, demonstrating the synergistic interaction between the Pt and MoO_x was achieved¹⁶, in which the presence of MoO_x species are responsible for hydrogen activation. These two distinct types of active sites have been proposed to create a bifunctional surface that can enhance the activity for reaction.

4.2. Determination of the structure-activity relationships

The characterization of Raman, combined with UV-vis and NH₃-TPD, show the dispersed MoO_x surface density is below approximately 6.19 Mo/nm², and MoO₃ crystallites appear above approximately 6.19 Mo/nm² due to oligomerization of some surface molybdate species. As shown in Fig. 14a, the Mo surface density covered by pseudo monolayer was estimated to be 3.5 Mo/nm² using the intercept of the two straight lines. For sub-monolayer coverages, the HDO reaction rate improved 26 times from 0.04 to 1.06 µmol s⁻¹ g⁻¹, followed by a decrease with further Mo addition that resulted in the formation of MoO₃ crystallites, as explained by the fact that dispersed Mo species as oxophilic active sites promote the deoxygenation whereas MoO₃ crystallites reduce the availability of reactive species for reactions. Fig. 14b shows the possible reaction mechanism. For Pt/MgO, the C-O bond was adsorbed on the Pt site and then broken in OPP, followed by the formation of BP. In the case of Pt/MoO_x/MgO, the feasible active sites for deoxygenation may be the interface between adjacent Pt and Mo species, which is in agreement with Pt-Mo catalysts for Water Gas Shift reaction⁶¹. The oxophilic sites represented by the coordination unsaturated MoO_x enhance the interaction of the oxygen in the dibenzofuran with the catalyst surface. Thus, the activation and cleavage of C-O bond adsorbed on the Mo sites can take place by spilt-over H-species resulting from the dissociation on the Pt particles, leading to the formation of BP after the dehydration of the reactive OPP, explaining the increase of HDO reaction rate in the hydrogenolysis of dibenzofuran.

5. Conclusions

In this work, we report the Pt/MoO_x/MgO catalysts that have high activity and selectivity for the HDO of dibenzofuran. The addition of oxophilic Mo species could significantly improve the HDO reaction rate which was increased 26 times from 0.04 μ mol s⁻¹ g⁻¹ (Pt/MgO) to 1.06 μ mol s⁻¹ g⁻¹ (Pt/7MoO_x/MgO). This could be related to the improved reducibility of the Pt species by electron transfer as confirmed by H₂-TPR, CO-IR and XPS, and an increase in acidic sites as confirmed by NH₃-TPD. The highest BP yield (100%) was obtained with Pt/7MoO_x/MgO in which the molybdate species formed a near monolayer on the support. echnology Accepted Manu

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The catalytic activity can be controlled by MoO_x surface density and vary with the increased MoO_x surface density MO_{2} voleamont shape manner. At low Mo coverage (< 2.27 Mo/nm²), the dispersed MoO_x species are dominant that promote the reaction activity, whereas the presence of crystallite MoO₃ at higher MoO_x surface density (> 6.19 Mo/nm²) reduces the availability of reactive MoO_x species, as evidenced by reactivity studies in combination with UV-vis, Raman and NH₃-TPD. DFT calculations further proved the existence of synergistic effect between Pt species in affording hydrogen species and neighboring MoO_x species in adsorbing/activating C-O bond. Thus, Pt/MoO_x/MgO is a promising catalytic system for HDO, and further optimization of its properties may lead to an effective catalyst for the HDO of oxygen-containing compounds.

Conflicts of interest

There are no conflicts of interest to declare.

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The catalytic performance of selective hydrodeoxygenation of dibenzofuran can be controlled by MoO_x surface density and varied with the increased MoO_x surface density in a volcano-shape manner.

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