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Article (Special Issue on Celebrating the 70th Anniversary of Dalian Institute of Chemical Physics, CAS)

Hydrodeoxygenation of anisole over different Rh surfaces

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ARTICLE INFO

Article history:

Received 10 January 2019

Accepted 7 March 2019

Published 5 November 2019

Keywords:

Hydrodeoxygenation

Anisole

Alkoxy

Oxophilicity

Phenolic

Surface defects

ABSTRACT

The cleavage of the alkoxy (Ar–O–R) ether bond present in anisole is an interesting hydrodeoxygenation (HDO) reaction, since this asymmetric group contains two different C–O bonds, C_{aryl}–O or C_{alkyl}–O, which could potentially cleave. Recent work on the HDO of anisole over Pt, Ru, and Fe catalysts has shown that a common phenoxy surface intermediate is formed on all three metals. The subsequent reaction path of this intermediate varies from metal to metal, depending on the metal oxophilicity. Over the less oxophilic Pt, phenol is the only primary product. By contrast, on the more oxophilic Fe catalyst, the sole primary product is benzene instead of phenol. On Ru, with intermediate oxophilicity, both benzene and phenol are primary products. In this contribution, we have investigated Rh catalysts of varying surface nanostructures. A combination of experimental measurements and computational calculations was used to explore the effects of varying metal coordination number, an additional parameter that can be used to control the oxophilicity of a metal. The results confirm that metal oxophilicity is a good descriptor for HDO performance of metal catalysts and it can be controlled via selection of metal type and/or metal extent of coordination. Small Rh metal clusters with low coordination metal sites are more active for the deoxygenation pathway but also quickly deactivated while large clusters with high coordination sites are more active toward hydrogenation and more stable.

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1. Introduction

Hydrodeoxygenation (HDO) is an effective reaction for upgrading biomass to fuels and chemicals [1]. For example, biomass pyrolysis oil contains significant fractions of phenolics and other oxygenated aromatic compounds derived from lignin, which require deoxygenation. Therefore, the HDO reaction of these biomass-derived compounds has attracted attention of researchers in recent years [2–5]. Transition metals are partic-

ularly active for the cleavage of C–O bonds, and a large number of studies have investigated catalysts containing different characteristics, such as varying types of metal [6,7], particle size and coordination number [8,9], alloying elements [10–15], supports [16–19], and bifunctionality in cooperation with the acidic function of zeolites [20–27].

The two most abundant functionalities in these oxygenated aromatic compounds are hydroxy (–OH) and alkoxy (–OR) groups. In previous studies on the removal of the –OH func-

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This work was supported by the U.S. Department of Energy, DOE/EPSCOR (Grant DESC0004600). The computational research used the supercomputer resources of the National Energy Research Scientific Computing Centre (NERSC) and the OU Supercomputing Centre for Education & Research (OSCER) at the University of Oklahoma.

DOI: S1872-2067(19)63345-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 11, November 2019

tionality in *m*-cresol, we have proposed that the metal's oxophilicity (described as the M–O bond strength) is a major descriptor of the HDO activity as well as the –OH removal mechanism [6]. That is, over less oxophilic metals, such as Pt or Pd, HDO proceeds via an indirect pathway involving tautomerization-hydrogenation-dehydration, while over more oxophilic metals (Ru, Fe, Rh), it happens via direct deoxygenation [6]. Oxophilicity is a direct function of the position of the *d*-band center with respect to the Fermi level. Therefore, it can be adjusted, not only by changing the type of metal used, but also by varying the coordination number of metal atoms [28–32]. For example, we have shown that small Rh clusters with higher density of low-coordination atoms are more active for –OH removal but also more prone to deactivation while larger Rh clusters with higher coordination numbers are less active but, at the same time, more stable [8].

The mechanism for the cleavage of the alkoxy (Ar–O–R) bond is more complicated than the corresponding to –OH due to the asymmetric nature of this ether group, which contains two different C–O bonds, C_{aryl}–O and C_{alkyl}–O. Cleavage of the C_{aryl}–O bond eliminates the oxygen functionality from the aromatic ring while cleavage of the C_{alkyl}–O leads to formation of a phenolic compound. In a recent work [7], we compared the HDO reaction of anisole over Pt, Ru, and Fe catalysts. No methanol was observed as a product on any of the three catalysts. Therefore, neither experimental nor density functional theory (DFT) calculations gave evidence that C_{aryl}–O or C_{alkyl}–O was cleaved initially, but rather the C–H bond in the methyl group was activated first. Only when the –CH₃ group was dehydrogenated enough, it was possible to break the C_{alkyl}–O bond. As a result, a common phenoxy surface intermediate, C₆H₅O* is expected to be formed on all three metals. However, the subsequent reaction path of this intermediate varies from metal to metal (Scheme 1). It was hypothesized that the mechanisms responsible for the different outcomes on the different metals are directly related to the metal oxophilicity [7]. Indeed, when the product ratio of phenol-to-benzene was compared as a function of anisole conversion over the three metals, a very diverse behavior is observed, as shown in Fig. S1. That is, over the less oxophilic Pt, a very high phenol-to-benzene ratio is observed at low conversions, but it becomes lower as conversion increases.

This trend indicates that Pt greatly favors hydrogenation of

Scheme 1. Reaction pathway for anisole conversion.

the phenoxy intermediate C₆H₅O* to phenol, which is the dominant primary product. As conversion increases phenol converts to benzene in a secondary path. This trend is in good agreement with our DFT calculations that showed an exceedingly high barrier for C_{aryl}–O cleavage of the phenoxy intermediate on Pt (270 kJ/mol). By contrast, the hydrogenation of the phenoxy intermediate has a much lower energy barrier and it produces phenol as the primary product (17 kJ/mol).

An opposite behavior is observed on the more oxophilic Fe catalyst, over which the phenoxy intermediate prefers to undergo direct C_{aryl}–O cleavage, producing benzene. On this metal, the phenol-to-benzene ratio is found to be zero at all anisole conversions, indicating that benzene rather than phenol is the only primary product. This is also in good agreement with the DFT calculations which show that the energy barrier for direct C_{aryl}–O cleavage (101 kJ/mol) is lower than that for hydrogenation (147 kJ/mol) of the phenoxy intermediate over Fe.

Finally, on a metal with intermediate oxophilicity like Ru, this ratio is in between those found on Pt and Fe, dropping with conversion. This trend shows that both benzene and phenol are primary products and more benzene is formed in a secondary path. This experimental trend was also in perfect agreement with DFT calculations, which showed that the energy barriers for C–O bond cleavage and hydrogenation of the phenoxy intermediate have comparable values, which are 165 and 134 kJ/mol, respectively.

In addition to the type of metal, the structure of metal surface also has significant impact on the C–O bond cleavage activity since coordination of surface metal atoms controls the metal oxophilicity. Metal catalysts with different metal cluster sizes such as Ni/SiO₂, Rh/SiO₂, Ru/NbOPO₄, etc. have been investigated for HDO activity of many different phenolic molecules [8,9,33,34]. A general trend was recently observed in which the smaller metal particles showed higher activity for C–O bond cleavage. In this contribution, we have further explored the influence of metal nanostructures on the HDO mechanism of anisole and its physical origin. By combining experimental measurements and DFT calculations, we investigate the effects of varying surface coordination number, a parameter that can be used to control the oxophilicity of a metal catalyst. Rhodium metal catalysts with different particle sizes have been chosen since Rh possesses intermediate oxophilicity between Pt and Fe; therefore the particle size effects would be more clearly discerned, as observed in our previous study with *m*-cresol [8]. Ru also possesses intermediate oxophilicity between Pt and Fe, but Ru is also very active for hydrogenolysis, giving high yields of methane [6,7]. Since the purpose of this work is to focus on the C–O bond cleavage activity at two positions C_{aryl}–O and C_{alkyl}–O, the best candidate for this study is Rh metal because it is active for C–O bond cleavage while its cracking activity is limited.

2. Experimental

2.1. Catalyst preparation

Three Rh/SiO₂ samples with different metal particle sizes

were prepared by incipient wetness impregnation of SiO₂ support (Hi-sil 210, BET area 135 m²/g) using Rhodium (III) nitrate aqueous solution (10 wt% Rh in > 5 wt% HNO₃, purchased from Sigma-Aldrich). The metal particle sizes were controlled using different metal loading and treatment conditions. That is, we made small Rh metal clusters with low metal loadings and mild treatment conditions, while we made large Rh clusters with high metal loading and more severe treatment conditions. After impregnation, the low-loading catalyst (0.6 and 2.5 wt% Rh/SiO₂) was heated under H₂ at 200 °C for 2 h, while the high-loading catalyst (7 wt% Rh/SiO₂) was heated under N₂ at 550 °C for 2 h, and then for an additional 12 h period at 550 °C under H₂ flow.

2.2. Catalyst characterization

The catalysts were characterized by high resolution transmission electron microscopy (HR-TEM) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed CO. The TEM samples were first dispersed in ethanol with a Cole-Parmer horn sonicator operating at 25% amplitude for 10 min and then deposited onto lacey carbon coated copper grids (300 mesh) before analysis on a TEM JEOL 2000 field emission system operated at 200 kV. DRIFTS of adsorbed CO was performed using a Perkin-Elmer Spectrum 100 FTIR spectrometer, equipped with a MCT detector. The diffuse reflectance cell is from Harrick Scientific, type HVC-DR2 equipped with CaF₂ windows for in-situ reduction. The IR spectra were taken at a resolution of 4 cm⁻¹, collecting 256 scans for each spectrum. In a typical DRIFTS experiment, the catalyst was reduced under H₂ for 1 h at 300 °C, then cooled down to room temperature under He flow and purged in He for 30 min. The background was recorded at this time. Prior to obtaining the scans, the catalyst was exposed to a flow of 5% CO in He for 30 min at room temperature and purged in He for 30 min.

2.3. Catalytic activity measurements

All catalytic tests were conducted using a micro-pulse reactor, which allows us to precisely monitor deactivation and study the catalytic activity, starting from a pristine surface and following with gradual deactivation after each consecutive pulse, as described elsewhere [8]. In a typical experiment, the catalyst (pellet size 250–350 μm) was packed in a vertical quartz tube reactor (20 cm L × 0.6 cm D) and pre-reduced in-situ under continuous flow of 100 sccm H₂ at 400 °C for 1 h. Subsequently, it was cooled down to the selected reaction temperature (270 °C), keeping the catalyst under H₂ flow during the entire experiment. Only a small amount of feed is introduced periodically through the catalytic bed. The products were analyzed online by GC (Agilent HP 5890) equipped with a FID detector and a HP-Innowax capillary column. The benefit of this type of reactor has been demonstrated in previous work, in which the device enabled us to directly observe structure/activity relationship on clean metal surfaces and how the product distribution changes as the surface gradually becomes deactivated [8].

2.4. DFT calculations

Plane-wave DFT calculations were performed using the Vienna *ab initio* Simulation Package (VASP) [35,36]. The Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) was used to calculate the exchange-correlation energy [37]. The vdW corrections were included using the DFT-D3 method [38]. The Rh(111) and Rh(533) surfaces were modeled with a lattice constant of 3.81 Å of the Rh bulk, close to a reported value of 3.803 Å [39]. A 4 × 4 unit cell of Rh(111) was chosen to minimize lateral interaction between neighboring anisole molecules. Both repeated slabs of Rh (533) and Rh (111) consisted of 80 Rh atoms with a vacuum space of 15 Å in the z-direction to separate successive layers. All of reactants, intermediates and products structures were optimized until the forces on each atom were less than 0.01 eV/Å. A kinetic cutoff energy of 400 eV was used in the calculations. The top two layers were allowed to fully relax in all calculations, whereas the bottom layers were fixed to the bulk distance of the metal. The adsorption energy of anisole on a Rh surface was defined as:

$$E_{ads} = E_{TOT}(anisole + surface) - E_{TOT}(anisole) - E_{TOT}(surface) \quad (1)$$

where $E_{TOT}(anisole + surface)$ is the DFT-calculated total energy of anisole adsorbed on the metal surface. $E_{TOT}(anisole)$ defines the total energy of an isolated anisole molecule, and $E_{TOT}(surface)$ is the total energy of the bare slab. The adsorption was analyzed at highly symmetric adsorption sites of the metal surface. Spin polarized calculations were performed for the atomic O and H atoms in the gas phase. Transition states were calculated using the Nudge Elastic Band (NEB) method [40–42], and verified by calculating the vibrational frequencies.

3. Results and discussions

3.1. Catalyst characterization

The three Rh/SiO₂ catalysts of different metal loading (0.6, 2.5 and 7 wt% Rh) and thermal pre-treatments were found to have varying particle sizes, as expected. As demonstrated in Fig. 1, HR-TEM analysis of the catalysts clearly reflects the different ranges of metal cluster sizes and shapes. The particle size decreases in the expected order (7 > 2.5 > 0.6 wt% Rh).

The corresponding histograms are summarized in Fig. 2. The 7 wt% Rh catalyst has particles that range in size up to about 7 nm with an average of 4 nm; by contrast, the 2.5 wt% Rh catalyst exhibits a much smaller average size (2 nm) and a range in which no particles are larger than 4 nm; finally, the lowest loading catalyst (0.6 wt% Rh) has a much narrower size distribution centered at 1 nm.

In correspondence with these differences in particle sizes, the DRIFT spectra of adsorbed CO exhibited a vastly different distribution of intensity of the characteristic IR absorption bands (Fig. S5). Table 1 summarized the relative intensities observed on two different samples with varying particle sizes for the three different modes, gem (G) dicarbonyl, linear (L), and bridge (B). The gem dicarbonyl band is typically used as a fingerprint for the presence of small Rh cluster, while the

Fig. 1. HR-TEM images of 7, 2.5 and 0.6 wt% Rh/SiO₂ catalysts.

bridge mode is a fingerprint for large Rh clusters. The gem twin band arises when two CO molecules adsorb on one Rh site; thus, the doublet represents the symmetric and asymmetric vibrations of the CO molecules. A linear band corresponds to one CO molecule adsorbed atop one Rh atom, while the bridge band appears when one CO molecule adsorbs on a multiplet of Rh atoms [43–47].

As reported in Table 1, over the small metal particles in the 2.5 wt% Rh catalyst, the gem bands have significantly more than a third of the intensity of the linear band, taken as a reference, indicating a very high density of low-coordination Rh sites. By contrast, they totally disappear on the 7 wt% Rh sample. On the other hand, the bridge band is less than 10% of the linear band on the 2.5 wt% Rh/SiO₂ catalyst, but it rises to 25% on the 7 wt% Rh sample, showing a good agreement with TEM results mentioned above. Due to the low loading, it was not possible to get a DRIFT spectrum with acceptable signal/noise for the 0.6 wt% Rh.

3.2. Catalytic conversion of anisole

Fig. 2. Particle size distribution of 7, 2.5 and 0.6 wt% Rh/SiO₂ catalysts.

Table 1

Relative Intensity of the DRIFTS bands of different CO adsorption modes on two Rh/SiO₂ catalysts of varying metal particle sizes.

CO adsorption mode	Gem (2030 and 2100 cm ⁻¹)	Linear (2050–2070 cm ⁻¹)	Bridge (1800–1900 cm ⁻¹)
2.5 wt% Rh/SiO ₂	35 and 42	100	6.4
7 wt% Rh/SiO ₂	—	100	25

3.2.1. C1 products from anisole

As mentioned above, along with the aromatic products (phenol and benzene), the HDO reaction of anisole also produces C1. If, as reported in the previous study, methane is the only C1 product obtained, the ratio of C1/C6-ring should be one, provided that no significant amounts of C1 products remain on the catalyst surface [7]. On the other hand, if methanol is also produced, one can expect that some of it may decompose to CO or CO₂, not detectable by FID.

As shown in Fig. 3, contrary to the previous observations, we do observe some methanol in the products of anisole conversion. While the observed amounts of methanol are much lower than those of methane, there is still a detectable fraction. At the same time, Fig. 4 shows the C1/C6-ring ratio for the three Rh catalysts at varying anisole conversion. In this case, C1 is calculated as the sum of the amounts of methane and methanol observed.

While the C1/C6-ring ratio is close to 1, there is a consistent difference among the three catalysts that is worth discussing. The highest and closest to 1 ratio is observed over the catalyst with large Rh cluster (7 wt% Rh). At the same time, this catalyst is the one that produces less methanol. By contrast, the catalysts with smaller Rh clusters (and rougher surfaces) not only produce more methanol, but also C1 products (CO, CO₂) that we cannot detect via FID. The formation of methanol suggests that anisole could undergo direct C–O bond cleavage on the metal

Fig. 3. Ratio of methanol/methane product at varying anisole conversion over the 0.6, 2.5, and 7 wt% Rh/SiO₂ catalysts at 270 °C.

Fig. 4. Ratio of C1/C6 ring product at varying anisole conversion over the 0.6, 2.5, and 7 wt% Rh/SiO₂ catalysts at 270 °C.

surface to produce benzene and methanol. Based on the descending order of C1/C6 ratio of 0.6 > 2.5 > 7 wt% Rh/SiO₂ as seen in Fig. 3, it seems that small Rh particles favor this pathway more than larger Rh particles. This reaction pathway will also be investigated in the DFT theoretical calculation section below.

3.2.2. Phenol and benzene production from anisole

Fig. 5 shows the yield evolution of the ring products obtained over the pristine 2.5 wt% Rh/SiO₂ catalyst from the first anisole pulse in the micro-pulse reactor as a function of catalyst mass. Since the independent variable in a pulse reactor is space time (W/F), one can vary space time by keeping mass constant and varying the flow rate, or vice versa. The three products are benzene, phenol and cyclohexane methyl ether.

The positive slope for all three products that can be observed near zero conversion, that is approaching zero mass of catalyst, indicates that they are all primary products. Also, the almost identical initial production of benzene and phenol re-

Fig. 5. Yield of benzene, phenol and cyclohexane methyl ether from anisole conversion in the first pulse as a function of mass of catalyst of 2.5 wt% Rh/SiO₂ at $T_{\text{rxn}} = 270$ °C.

flects the similar rates of the phenoxy intermediate to either hydrogenation to phenol or deoxygenation to benzene.

Since Rh has an intermediate oxophilicity, similar to Ru metal, it is reasonable that both reaction paths are comparable. Interestingly, for this catalyst, the phenol-to-benzene ratio only starts decreasing at high conversion (larger mass). The third observed (minor) product, cyclohexane methyl ether, arises from the hydrogenation of the aromatic ring of anisole, without C–O or C–C cleavage. Clearly, this is a much less preferred reaction pathway.

Fig. 6 compares products selectivity at the same anisole conversion (10%) over the three different Rh catalysts. The data is taken from the first pulse of anisole through the catalyst bed. Thus, it represents the activity of pristine surfaces. We can see that as the Rh metal cluster size decreases from 4 > 2 > 1 nm for 7 > 2.5 > 0.6 wt% Rh, respectively, the selectivity to phenol and its derivatives (cyclohexanol and cyclohexanone) decreases while the selectivity to benzene and its derivatives (cyclohexane) increases. As mentioned above, at such a low anisole conversion benzene is only formed by primary HDO of anisole. That is, this selectivity represents the preference of the phenoxy intermediate to undergo either hydrogenation to phenol or deoxygenation to benzene on each Rh surface. Clearly, smaller Rh clusters with a higher density of surface defects (steps, kinks) exhibits a higher selectivity to deoxygenation while larger Rh clusters with smooth surfaces (terraces) favor hydrogenation of the phenoxy intermediate to phenol.

To further confirm the above observation, we compared the number of anisole turnovers per exposed Rh site as a function of the number of pulses over the three different catalysts. The number of turnovers was calculated as the moles of anisole converted in each pulse to a specific product relative to the moles of surface Rh atoms present in the catalyst. These numbers are compared in Fig. 7 for the three Rh catalysts of different particle sizes. It can be seen that, regardless of the small changes in activity exhibited after each consecutive pulse, the specific phenoxy hydrogenation activity increases with particle size, while, by contrast, the specific phenoxy deoxygenation activity decreases with particle sizes. Fig. 7 also illus-

Fig. 6. Products selectivity of 10% anisole conversion over different Rh catalyst including 7, 2.5 and 0.6 wt% Rh/SiO₂ at $T_{\text{rxn}} = 270$ °C.

Fig. 7. Number of turnovers of anisole per exposed Rh site to different products; that is, phenol, benzene and their derivatives at increasing number of pulses over the three catalysts 0.6, 2.5, and 7 wt% Rh/SiO₂ at 270 °C.

trates the extent of catalyst deactivation as a function of number of anisole pulses sent over the catalyst. While no significant deactivation is observed for the phenoxy hydrogenation pathway, the drop in activity for deoxygenation, particularly on the smallest Rh cluster 0.6 wt% Rh/SiO₂ is significant during the initial pulses.

Apparently, the 0.6 wt% Rh/SiO₂ catalyst contains very active sites for deoxygenation of the phenoxy intermediate, but they are prone to deactivation. On the other hand, the 2.5 and 7 wt% Rh catalysts contain less active but more stable sites. Finally, it is observed that hydrogenation is not significantly deactivated in any of the catalysts. As previously proposed, deoxygenation of the phenoxy intermediate on the more oxophilic sites also produces O* species, which need to be removed to regenerate the active site. Our DFT calculations have shown that the energy barriers necessary to remove the thus generated surface O* via hydrogenation are higher on low-coordination sites on the stepped surface Rh(533) than on flat high-coordination terraces Rh(111), which agrees with the experiments [8].

3.3. DFT calculations on Rh(111) and Rh(533)

3.3.1. Adsorption of anisole on Rh(111) and Rh(533)

In the following we apply DFT calculations to investigate the adsorption and reaction of anisole on Rh(111) and Rh(533) surfaces. The former is an approximate model of the flat surfaces in larger particles, while the latter represents the low-coordination stepped surfaces in small nanoparticles. Fig. S2 shows the side view of anisole adsorption on the terrace Rh(111) and the step of the Rh(533) surface. Adsorption of anisole on Rh(111) favors a bridge configuration with an adsorption energy of −283 kJ/mol, followed by the hcp hollow site. In the lowest energy configuration, anisole lays flat on the surface with the six-carbon atom ring shared amongst four Rh surface atoms and the O–CH₃ group tilted away from the surface. The distance between the oxygen atom and the Rh(111) surface is 2.98 Å. On the Rh(533) surface, anisole tends to ad-

sorb with the O–CH₃ away from the rhodium atoms on the step (Fig. S2), probably caused by steric hinderance. However, the oxygen atom forms a covalent bond of 2.6 Å with the step Rh atom, a configuration that favors deoxygenation, as discussed below. The adsorption energy of Rh(533) is −278 kJ/mol. Previous studies have shown that though “atop” sites are unfavorable, they can be favored in defected surfaces [48]. Notice that anisole adsorption on Rh(533) is weaker than on Rh(111). This difference may be due to two possible reasons: first, the presence of the step results in a lower number of carbons attached to the surface than on the flat terrace; and second, the oxygen proximity to the step does not make up for the loss of about three C–Rh bonds, as seen in Fig. S2. Previous studies on phenol support this explanation, showing that it adsorbs more favorably on Rh(111) terraces than on Rh(211) stepped surfaces [49].

3.3.2. Reaction path of anisole HDO on Rh(111)

The energy barriers and reaction energies for different reaction pathways of anisole on Rh(111) are shown in Fig. 8. We first considered direct C–O bond cleavage on the surface. One proposed pathway is to directly cleave the methyl (–CH₃) over Rh(111). This pathway turns out to be thermodynamically favorable with reaction energy of −19 kJ/mol but it remains kinetically unfavorable with a high activation barrier of 258 kJ/mol. The C_{aryl}–O bond may also be directly cleaved to form a phenyl intermediate, which could then be hydrogenated to benzene. In order to cleave –OCH₃ from anisole on Rh(111), the C_{aryl}–O bond increases from 1.37 Å in the reactant to 1.93 Å in the transition state. The activation barrier is also very high at 226 kJ/mol for this endothermic (89 kJ/mol) reaction.

We have discussed above the possibility of sequentially dehydrogenating the –CH₃ moiety before the C–O cleavage. Indeed, as shown in Fig. 8, the first –H removal is more favorable with an activation barrier of 175 kJ/mol, which is much lower than those for demethylation or demethoxylation. Fig. S3 compares energy barriers and energy of reactions for three different possible pathways of anisole on Rh(111), which clearly

Fig. 8. Layout of DFT calculated reactant, transition state and product structures for C_{aromatic}–O bond breaking, C_{alkyl}–O and dehydrogenation reactions of different Ph–O–CH_x (1 ≤ x ≤ 3) on Rh(111) surface. (Activation energy/energy of reaction).

demonstrates that dehydrogenation is the most favorable pathway. After the first H removal, we analyze the possible paths for Ph-O-CH_2^* , which could be cleaved at the $\text{C}_{\text{alkyl-O}}$ or the $\text{C}_{\text{aryl-O}}$, or could lose a second H. We find that the second dehydrogenation has an energy barrier of 91 kJ/mol, which is lower than 137 and 196 kJ/mol for the other pathways. This successive dehydrogenation is both kinetically and thermodynamically favorable (indicated by the green arrows in the figure).

As seen in the reaction scheme of Fig. 8, removing the 3rd H-atom would create a carbon that needs to bind three rhodium atoms. It would in turn have to shift the whole molecule to accommodate for this highly reactive product. This third dehydrogenation is significantly more difficult with an activation barrier of 166 kJ/mol on Rh(111). Instead, the Ph-O-CH^* can now be cleaved at the $\text{C}_{\text{alkyl-O}}$ bond, which forms a thermodynamically stable product with a reaction energy of -55 kJ/mol and a lower activation barrier of 143 kJ/mol. Successive dehydrogenation of the $-\text{CH}_3$ on Rh(111) has significantly reduced the energy requirement to form a phenoxy intermediate, similar to the reaction mechanisms described before on Pt(111) and Ru(0001) [7]. Also, demethoxylation is almost always kinetically unfavorable, which is in line with our experimental results showing that only a small amount of methanol is formed.

3.3.3. Reaction paths for HDO of anisole over Rh(533)

In the following we discuss reactions on the stepped surface Rh(533), which exhibits similar pathways as the more oxophilic metals previously studied, i.e. Ru(0001) and Fe(110) with some subtle differences. As we did for the flat surface, we first consider direct cleavage of the anisole C–O bonds on the stepped surface. Similar to the case on Rh(111), the $\text{C}_{\text{aryl-O}}$ bond on Rh(533) stretches from 1.42 Å to 1.70 Å in the transition state with an energy barrier of 141 kJ/mol. This value is a significantly lower compared to 226 kJ/mol observed for the terrace surface. It is also lower than the previously reported values for Pt(111) (258 kJ/mol) but higher than those for Ru(0001) (99 kJ/mol) and Fe(110) (79 kJ/mol) [7]. Upon cleavage, the $-\text{OCH}_3$ binds atop of one Rh atom to form a Rh–O bond with length of 2.15 Å. The barriers for demethoxylation and demethylation are very similar, both of them lower than the corresponding values calculated for Rh(111).

As shown in Fig. 9, removal of one H-atom from $-\text{CH}_3$ remains a favorable pathway with a much lower activation barrier than the two previous pathways. With an energy barrier of 79 kJ/mol, Rh(533) can catalyze the successive dehydrogenation of anisole to remove the first H-atom. However, unlike the reactions on Rh(111), due to the high reactivity of Rh(533), C–O bond cleavage can occur after the first dehydrogenation, rather than after the second one as was the case for Rh(111), to form the crucial surface phenoxy intermediate. The preferred steps are shown with green arrows, in Figs. 9 and S4.

To compare these calculations with the experimental observations, we note that on catalysts with small Rh nanoparticles we observed higher yields of deoxygenation products. The DFT calculations show that, although on the stepped surface

Fig. 9. Layout of DFT calculated reactant, transition state and product structures for $\text{C}_{\text{aromatic-O}}$ bond breaking, $\text{C}_{\text{alkyl-O}}$ and dehydrogenation reactions of different Ph-O-CH_x ($1 \leq x \leq 3$) on Rh(533) surface. (Activation energy/energy of reaction).

the most favorable path is dehydrogenation followed by $\text{C}_{\text{alkyl-O}}$ cleavage to form the phenoxy, we find relatively low barriers for the direct cleavage of the $\text{C}_{\text{aryl-O}}$ bond of adsorbed anisole (141 kJ/mol), which leads to the formation of benzene and methanol. This is in line with the experimental observations of higher methanol to methane ratio on the smaller nanoparticles (Fig. 3). This relatively lower barrier for $\text{C}_{\text{aryl-O}}$ bond cleavage may be explained in terms of oxophilicity of the metal.

Specifically, we have found that the Rh(533) surface has higher affinity for oxygen atoms than Rh(111), Pt(111) and slightly lower than Ru(0001). It is well known that oxophilicity of metals is determined by their individual *d*-bands. In this case, the differences between the flat terraces and stepped surfaces are very clear. Fig. 10 shows that the density of states of the Rh(533) step atoms becomes narrower and sharper and shifts towards the Fermi level; this upshifted *d*-band can explain the enhanced adsorption of oxygen at the step atoms, which helps cleaving the C–O bond as the Rh–O interaction becomes

Fig. 10. Density of states for a step atom on Rh(533) (blue curve) and from a terrace atom on Rh(111) (orange curve). *d*-band centers calculated as: -1.8 eV for Rh(111) and -1.5 eV for Rh(533).

Fig. 11. Side view and top views of DFT calculated reactant, and product structures for deoxygenation/hydrogenation of phenoxy intermediate on Rh(111) terrace surface. (Activation energy/energy of reaction).

stronger. Experimentally, this is the case observed with the catalysts containing smaller metal particles, which are shown to contain a higher density of steps, edges and other low-coordination sites.

3.3.4. Reactions of the phenoxy intermediate

Once anisole has been sequentially dehydrogenated, a surface phenoxy remains as a crucial intermediate, on both the Rh(111) and Rh(533) surfaces. As demonstrated in Scheme 1, this intermediate can undergo either hydrogenation to form phenol or direct $C_{aryl}-O$ cleavage to form surface phenyl, which subsequently hydrogenates to become benzene. In the following we analyze the surface reactions of the phenoxy species.

Experiments carried out by Pasco *et al.* [50] showed that activation barriers for adsorption of hydrogen on Fe (111), (100), (110) surfaces were relatively low, averaging 48 kJ/mol. Therefore, the rate limiting step for hydrogenation should be the actual surface reaction of the $Ph-O^*$ intermediate and H^* to obtain phenol. As shown in Fig. 11, over Rh(111) surface, hydrogenation of phenoxy is slightly exothermic while deoxygenation is endothermic. The energy barrier to hydrogenate the surface phenoxy on Rh(111) is 136 kJ/mol, much lower than that for deoxygenation (190 kJ/mol). This explains why we observed phenol as the main product resulting from the surface phenoxy on catalysts with larger Rh particles. At the same time, DFT calculations show that hydrogenation on Rh(111) is less favorable than on Pt(111) which was found to be 17 kJ/mol. On the other hand, this value is about the same as that found for Ru(0001), 134 kJ/mol, less than that for Fe(110), 147 kJ/mol.

By contrast, as shown in Fig. 12, the energy barrier to hydrogenate the surface phenoxy on Rh(533) is 166 kJ/mol, which is higher than that for deoxygenation on this surface (155 kJ/mol). This explains the experimental trend shown in Fig. 6 with the benzene-to-phenol ratio increasing with decreasing size of Rh nanoparticles.

Fig. 12. Side view and top views of DFT calculated reactant, and product structures for deoxygenation/hydrogenation of phenoxy intermediate over Rh(533). (Activation energy/energy of reaction).

Fig. 13. Correlation between activation energies for deoxygenation of surface phenoxy ($Ph-O^*$) on different metal surfaces and the oxophilicity (O-affinity).

By combining previous experimental and theoretical results on Pt, Ru and Fe catalysts [7] with the current observations we can conclude that metal oxophilicity serves as a good descriptor for the HDO activity and selectivity of metals. That is, hydrogenation follows the trend $Pt(111) > Rh(111) > Rh(533) > Ru(0001) > Fe(110)$, while the opposite trend is found for the deoxygenation reaction. Remarkably, both trends correlate with the oxophilicity of the metal. Fig. 13 shows that the values obtained in the current calculations for the different surfaces of Rh are in excellent match with the correlations previously found for Pt, Ru and Fe metal catalysts.

4. Conclusions

It is clearly shown here that metal oxophilicity is a good descriptor for HDO performance of metal catalysts and, more importantly, it can be manipulated by changing the *d*-band center, which in turn can be tailored via changing either the metal type or the coordination of metal atoms. The experimental results obtained with metal nanoparticles of varying sizes are in good agreement with DFT calculations, which use Rh(111) to demonstrate terraces in large metal clusters and Rh(533) to represent step sites in small metal clusters. Over Rh metal catalyst, the most energetically favorable pathway of anisole is to form a phenoxy intermediate, which can later undergo either hydrogenation to phenol or deoxygenation to benzene. Small Rh metal clusters with low coordination metal sites are more active for the deoxygenation pathway but also quickly deactivated while large clusters with high coordination sites are more active toward hydrogenation and more stable. The formation of small amounts of CH_3OH suggests that a small fraction of anisole can undergo direct $C_{aryl}-O$ cleavage, which is not energetically favorable but still possible, especially on small Rh clusters.

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Graphical Abstract

Chin. J. Catal., 2019, 40: 1721–1730 doi: S1872-2067(19)63345-0

Hydrodeoxygenation of anisole over different Rh surfaces

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Manipulating the surface coordination of rhodium atoms can greatly affect the metal oxophilicity and in turn control its activity for C–O bond cleavage. In the hydrodeoxygenation of anisole, a step surface favors deoxygenation to benzene while a smooth terrace prefers hydrogenation to phenol.

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不同Rh表面上苯甲醚加氢脱氧

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摘要: 苯甲醚中烷氧基(Ar-O-R)醚键的断裂是一个有趣的加氢脱氧反应, 因为这个不对称的基团包含两个不同的C–O键, C_{aryl}–O或C_{alkyl}–O, 它们可能会断裂。最近有关在铂、钌和铁催化剂上苯甲醚HDO的研究表明, 在所有三种金属上都形成了一种共有的苯氧基表面中间体。该中间体的后续反应路径因金属而不同, 这取决于金属的亲氧性。在亲氧性较低的铂上反应, 苯酚是唯一的主要产物。相反, 在亲氧性较强的铁催化剂上, 唯一的初级产物是苯而不是苯酚。在亲氧性适中的Ru上, 苯和苯酚都是主要产物。本文研究了不同表面纳米结构的铑催化剂。采用实验测量和理论计算相结合的方法, 研究了用来控制金属亲氧性的参数, 即金属配位数的影响。结果证实了金属亲氧性是描述金属催化剂催化HDO性能的很好的指标, 它可以通过选择金属类型和/或金属配位程度来加以控制。含低配位数的金属位的小Rh金属簇合物对脱氧路径活性更高, 但很快失活, 而含高配位数的大的簇合物对加氢活性更高, 且更加稳定。

关键词: 加氢脱氧; 苯甲醚; 烷氧基; 亲氧性; 酚类; 表面缺陷

收稿日期: 2019-01-10. 接受日期: 2019-03-07. 出版日期: 2019-11-05.

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