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# Insights into the role of nanoalloy surface composition toward catalytic acetone hydrogenation<sup>+</sup>

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Zhao Yang <sup>a</sup>\*, Huaze Zhu<sup>b</sup>, Huijuan Zhu<sup>a</sup>, Yanbing Wang<sup>a</sup>, liming Che<sup>a</sup>\*, Zhiqing Yang<sup>b</sup>\*, Jun Fang<sup>c</sup>, Qi-Hui Wu<sup>c</sup>, Bing Hui Chen<sup>a</sup>\*

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A significant composition-dependent catalysis behavior was observed in catalytic acetone hydrogenation. Carbon supported PtRu alloy nanoparticles (NPs) with optimal surface composition achieved ultra efficient and highly selective production of isopropyl alcohol.

Rational design of highly effective heterogeneous catalyst depends on the fundamental understanding of the structureproperty relationship in catalysis. Since the properties of the catalyst surfaces are closely correlated with the catalytic performance, the precise modification of the metallic catalyst surface by introducing another component could facilitate the controlled tuning of the performance.<sup>1-12</sup> Generally, alloy materials have distinct binding properties with reactants in contrast to those for monometallic materials.  $^{11}\ \mbox{Addition}\ \mbox{of}$ another metal can alter the availability of active surface sites (i.e., the ensemble effect) or the binding strength of reactants, intermediates, products, and spectator species (i.e., the electronic and/or strain effect).<sup>12</sup> The ratio between alloying components plays an important role in defining the physical and chemical properties of alloy materials,<sup>10</sup> a study on the surface chemistry and catalytic properties of the alloy catalysts with various compositions would be an important supplement to elucidate the underlying structure-property relationship.

Catalytic hydrogenation of carbonyl groups is one of the most useful and widely applicable reactions routes for organic synthesis.<sup>8</sup> In particular, acetone hydrogenation to isopropyl alcohol (C=O hydrogenation), plays important roles and has been applied in the renewable energy technology such as the chemical heat pumps (isopropyl alcohol-acetone-hydrogen chemical heat pump), H<sub>2</sub> storage schemes and DIPA (direct

isopropyl alcohol) fuel cells, which require a higher selectivity to isopropyl alcohol at high conversion than that presently available.<sup>13-15</sup> There are a range of heterogeneous or homogeneous catalysts reported in acetone hydrogenation (Table S1<sup>+</sup>). However, more efforts towards the production of isopropyl alcohol with an efficient but green method should be continuously demonstrated. Herein, we report the surface composition-controlled carbon supported PtRu nanoalloy catalyst for enhancing catalytic performance in acetone hydrogenation. It is worth mentioning that such present system shows green process and unexpected high efficiency relative to most of the current records (see ESI<sup>+</sup>). Catalytic activity and selectivity exhibit evident dependence on the atomic scale distribution of surface Pt and Ru sites, this composition-dependent behavior results from the essential distinction of functionality between these two metals on activating the reactants, and their complementary advantages in catalysis. Moreover, hydrogenation of 3-pentanone was also studied to underline the potential of the catalyst and such composition effect it could have on other carbonyl hydrogenation (of ketones) reactions.

A series of carbon black supported Pt-Ru bimetallic catalysts with fixed total theoretical metal loading but with various respective metal contents were prepared via a surfactant-free ethylene glycol reduction process (labeled as xPtyRu/C, where x and y denote the theoretical weight percentage loading of Pt and Ru, percentage sign was removed, see ESI<sup>+</sup>). These as-obtained bimetallic samples with seven different compositions show the similar structure of N<sub>2</sub> adsorption-desorption isotherms (Fig.S2<sup>+</sup>). Parameters including the BET surface area, total pore volume and average pore diameter are smaller than those of the parent catalyst's support, owing to the introduction of the guest metal NPs into the hole structure (Table S2<sup>+</sup>). As shown in Fig.1a, 3Pt/C and 3Ru/C exhibit the existence of typical metallic diffraction peaks which are indicative of the crystalline structure of metallic bulk Pt and Ru respectively by comparing with the reference patterns (ICDD-JCPDS Card No. 040802 and No.06-0663). Compared with Pt (111) in 3Pt/C, as the added Ru component's proportion in metal loading increases, the shape of the strongest diffraction peak in

<sup>&</sup>lt;sup>a</sup>Department of Chemical and Biochemical Engineering, National Engineering Laboratory for Green Productions of Alcohols-Ethers-Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. Email: zyang@stu.xmu.edu.cn (Z. Yang), Imc@xmu.edu.cn (L.M. Che), chenbh@xmu.edu.cn (B.H. Chen)

<sup>&</sup>lt;sup>b</sup>Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China. Email: yangzq@imr.ac.cn (Z.Q. Yana)

College of Chemical Engineering and Materials Science, Quanzhou Normal University, Quanzhou 362000, China.

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**Fig.1** XRD patterns, elemental line-scan and mapping results. a) XRD patterns of catalysts with various compositions. b) Partial enlarged view of XRD patterns. c) HAADF-STEM, elemental line-scan and mapping analysis of 1.5Pt1.5Ru/C.

bimetallic sample becomes increasingly broader. Similarly, the diffraction peak becomes broader than monometallic 3Ru/C as Pt proportion in metal loading increases. Result indicates the second metal component addition can result in the increase of diffraction peak's full width at half maximum (FWHM), which is derived from the decrease of metal particle diameter. Fig.1b shows the partial enlarged view of XRD patterns. In contrast with Pt (111) in 3Pt/C, the position of diffraction peak in bimetallic sample shifts to higher angle since Ru component added. Moreover, the degree of such diffraction peak position movement gradually increases with the proportion of Ru component in metal loading. Comparing with Ru (101) peak, the diffraction peak of bimetallic sample shifting to lower angle is observed since Pt component added. Results indicate the Pt-Ru alloy formation. Considering the different atomic size (Pt > Ru), a certain number of Ru atoms diffuse into the Pt lattice, which leads to a compressive strain (i.e., a contraction of the original lattice) for the original Pt fcc structure and thus results in diffraction peak position shifting to higher angle.<sup>16</sup> As the Ru proportion in metal loading increases, more Ru atoms diffuse into the Pt lattice, which leads to the larger degree of such peak position movement. Similarly, introduction of Pt into Ru leading to peak position shifting to lower angle is due to Pt atoms diffusing into the Ru lattice, resulting in a tensile strain

(i.e., a dilatation of the original lattice) of the original pure Ru lattice.<sup>16</sup> Fig.1c shows the elemental line-scan and mapping analysis results. The curve of intensity variation of Pt is similar in shape with that of Ru (line-scan analysis). Mapping results demonstrate that such two kinds of elements are uniformly mixed in Pt-Ru NPs due to the alloy formation.

A "V"-type variation behaviour with increased loading ratio of Pt to Ru is observed on metal particle diameter (Table S2<sup>+</sup>), which is consistent with the trend of shape variation in XRD diffraction peak described above. Many literatures reported the similar phenomenon that introduction of a second metal component can lead to the increase of bimetallic particle dispersion which attributes to the interplay between the two metal components.<sup>4,17-18</sup> In this study, such interaction derives from the alloy formation. Pt and Ru atoms diffuse into each other's lattice, the uniform mixing and mutual contact provide the availability for their interplay. When the proportion of second metal component in loading increases, the contact range between such two types of metal atoms would be enlarged and consequently leads to their interaction being strengthened, thus resulting in the metal particle dispersion further increase.

As two kinds of important solid surface analysis techniques, High-sensitivity low-energy ion-scattering spectroscopy (HS-LEISS) has an outstanding sensitivity toward the outermost atomic layer, whereas X-ray photoelectron spectroscopy (XPS) can probe the composition of NPs up to a few monolayers.<sup>19</sup> The variation in the area of elemental characteristic peak can express the changes in the quantity of the corresponding element on NPs surface.<sup>20-22</sup> In Fig.2, the consistence between HS-LEISS and XPS results is observed in the variation trend of characteristic elemental peak's area. 3Pt/C and 3Ru/C possess larger characteristic peak areas (for the corresponding metal) than other bimetallic samples'. As the proportion of second metal component in loading increases, there is an interactive variation behaviour observed between such two elements' characteristic peak areas (in both HS-LEISS and XPS). From 3Pt/C to 1.5Pt1.5Ru/C, Pt characteristic peak area decreases gradually accompanied with the increase of Ru peak area. Contrarily, from 3Ru/C to 1.5Pt1.5Ru/C, Pt peak area increases gradually with the decrease of Ru peak area. Results indicate that these seven samples possess the seven different surface element concentration ratios of Pt to Ru respectively. Variation trend in the metal component's characteristic peak area among these seven samples is consistent with that in the corresponding metal component's loading detected by ICP (Table S2<sup>+</sup>), illustrating the trend of variation in bulk phase composition is consistent with that in surface composition.

Catalytic performance in acetone hydrogenation substantially depends on the alloy's composition. A volcano type variation behaviour with increased loading ratio of Pt to Ru was observed in catalytic activity (see Table 1). With the optimum alloy composition (i.e., 1.5Pt1.5Ru/C), both catalytic conversion and TOF could reach their maximum values. Significantly, variation tendency of catalytic activity observed in acetone hydrogenation is exactly the same as that found in 3-pentanone hydrogenation, confirming the objectivity for the

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**Fig.2** HS-LEISS, XPS results and catalyst structure illustrations. (a) 3Ru/C, (b) 2.5Ru0.5Pt/C, (c) 2Ru1Pt/C, (d) 1.5Pt1.5Ru/C, (e) 1Ru2Pt/C, (f) 0.5Ru2.5Pt/C and (g) 3Pt/C.

important role of alloy composition in catalytic ketone's carbonyl hydrogenation. For the catalytic selectivity in acetone hydrogenation, Introduction of Ru into Pt could increase the selectivity to isopropyl alcohol and that kept increasing as the proportion of Ru in metal loading increased. 1.5Pt1.5Ru/C exhibited 100% selectivity to isopropyl alcohol, further increase of Ru proportion could not change the 100% selectivity to isopropyl alcohol, indicating the diisopropyl ether generation can be restricted when catalyst possesses more Ru than Pt (proportion in metal loading).

Alloy formation lets such two sites be uniformly mixed and present on the surface. Alloy sites usually show two features in the ensemble effect for the improvement of performance: 1. synergetic behaviour; 2. complementary advantages.<sup>4</sup> Since Pt and Ru all possess the capability to activate such two reactants (i.e., hydrogen and ketone),<sup>23-24</sup> rather than an absolute synergetic behaviour (hydrogen and ketone could be activated simultaneously and separately by different metals), the alloy showing higher activity tends to be attributed to the complementary advantages between Pt and Ru on activating the reactants. Catalytic ketone hydrogenation accords with Langmuir-Hinshelwood mechanism that the reaction rate is determined by the coverage of the two substrates on catalyst's surface.<sup>23,25</sup> Comparing with Ru, Pt has more affinity toward H<sub>2</sub>

**Table1** Catalytic performances of carbon supported PtRu nanoalloy catalysts with various compositions.

	Acetone			3-pentanone	
Catalyst	hydrogenation <sup>(a)</sup>			hydrogenation <sup>(c)</sup>	
	Conv.	Sel.	TOF	Conv.	TOF
	(%)	(%) <sup>(b)</sup>	(s <sup>-1</sup> ) <sup>(d)</sup>	(%)	(s <sup>-1</sup> ) <sup>(d)</sup>
3Pt/C	6.22	95.80	9.35	5.61	1.76
2.5Pt0.5Ru/C	37.40	97.58	23.53	27.40	3.83
2Pt1Ru/C	70.34	99.71	37.19	48.92	4.91
1.5Pt1.5Ru/C	100	100	46.39	77.62	6.57
1Pt2Ru/C	86.61	100	28.23	48.59	2.96
0.5Pt2.5Ru/C	56.01	100	16.58	35.01	1.74
3Ru/C	24.26	100	5.62	19.35	0.95
С	0	-	-	0	-
catalyst-free	0	-	-	0	-

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The reaction pathways are shown in Scheme S1<sup>+</sup>. <sup>a</sup> Reaction conditions: T=28 <sup>o</sup>C, P(H<sub>2</sub>)=5.3 MPa, 100 mg catalyst, 10 ml acetone, reaction time=6 min, agitation speed=500 rpm. <sup>b</sup> Selectivity to isopropyl alcohol, by-products are diisopropyl ether and water. <sup>c</sup> Reaction conditions: T=50 <sup>o</sup>C, P(H<sub>2</sub>)=5.3 MPa, 100 mg catalyst, 10 ml 3-pentanone, reaction time=20 min agitation speed=500 rpm. The main product is 3-pentanol (100% selectivity), no by-product was detected. <sup>d</sup> Conversion was maintained below 15%, the related conversion values and experimental details for TOF calculations are shown in Fig.S4<sup>+</sup>. Effect of agitation speed and catalyst's amount on catalytic activity are shown in Figs.S5-S6<sup>+</sup>. Results of reactions at different time on stream are shown in Fig.S7<sup>+</sup>.

due to the higher heat of adsorption of  $H_2$  than Ru.<sup>19</sup> Ru possesses more affinity toward carbonyl due to Ru is more oxophilic than Pt.<sup>19,26</sup> The coverage of the two adsorbates on Pt surface is different from that on Ru surface, thus resulting in their different catalytic reaction rates. Variation in the atomic scale distribution of Pt and Ru sites could lead to the coverage changes of such two adsorbates. A proper surface composition (i.e., 1.5Pt1.5Ru/C), could lead to an optimal coverage between such two kinds of substrates adsorbed on surface and bring the maximum activity. Higher or lower surface sites ratio of Pt to Ru may break the optimal multiple sites status and lead to the activity decrease.

Highly unsaturated surface Pt defect sites are responsible for the diisopropyl ether generation.<sup>27</sup> Catalytic selectivity to diisopropyl ether decreased with the proportion of Pt in metal loading (evaluation results). The decrease of Pt proportion in metal loading leads to the decrease of whole surface Pt concentration (HS-LEISS and XPS), consequently resulting in the decrease of surface concentration of Pt atoms located at the highly unsaturated defect sites (i.e., vertex and edge) and thus restricting the by-product's generation. When catalyst possesses more Ru than Pt (proportion in metal loading), the resultant 100% selectivity to isopropyl alcohol is attributed to the concentration of such by-product generation site is nearly negligible.

Metal particle sizes and metal loadings for the spent catalysts after acetone/3-pentanone hydrogenation reactions are shown in Fig.S8<sup>+</sup> and Table S3<sup>+</sup> respectively. Slight metal

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leaching was observed in the spent catalyst after the hydrogenation reaction. No evident difference was found in NPs size for the spent catalyst compared with fresh one. Valence states of fresh and spent catalysts (before/after hydrogenation reaction) were determined by XPS. There is no obvious change observed in valence distribution for spent catalyst in contrast to the fresh one. It is known that the presence of surface Ru4+ species facilitates the carbonyl activation.<sup>16,23</sup> Thus, to confirm the possible positive role of such Ru<sup>4+</sup> species, we performed the reduction treatment for the fresh catalyst to remove it (Figs.S9-S10<sup>+</sup>), as a result, the decrease of catalytic activity was observed after the catalyst's reduction treatment (Fig.S11<sup>+</sup>). The decreased activity when Ru<sup>4+</sup> is absent is due to its role of Lewis acid sites that are able to interact with the oxygen atom of the carbonyl bond (polarization of carbonyl),<sup>23</sup> in the case of its presence, improvement of hydrogenation rate would be favoured.

In conclusion, carbon supported PtRu nanoalloy catalysts with seven different surface compositions were synthesised and evaluated in hydrogenation of acetone. The observed strong dependence of catalytic performance on surface composition originates from the different catalytic properties between the two metals and their complementary advantages in catalysis. Similar catalysis behavior found in 3-pentanone hydrogenation verifies the objectivity of the structure-property relationship revealed in this study (I.e., the composition effect), which could assist the rational design of catalyst used in many other carbonyl compounds hydrogenation reactions (e.g., cellulose biomass, glucose, aldehydes, carboxylic acid, esters, etc.).

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Ultra efficient and green catalysis for acetone hydrogenation: boosting the catalytic performance by adjusting the nanoalloy surface composition.