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Selective ring opening of methylcyclopentane over surface-decorated Ir–Co bimetallic catalysts synthesized by galvanic replacement reaction

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Surface-decorated Ir–Co bimetallic catalysts were synthesized by a modified galvanic replacement reaction and evaluated by the selective ring opening (SRO) of methylcyclopentane (MCP). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was utilized to characterize the catalyst synthesis process, and H<sub>2</sub>-temperature-programmed reduction (H<sub>2</sub>-TPR) was performed to characterize the reduction behavior of the calcined catalysts and oxidation resistance of the reduced catalysts. Transmission electron microscopy (TEM) analysis was used to characterize metallic particle size distribution. The reactor evaluation results show quite different behaviors in conversion and product selectivity of the surface-decorated Ir–Co/SiO<sub>2</sub> and monometallic Ir/SiO<sub>2</sub>. At optimized Ir content, MCP conversion and mass-specific rate of SRO are significantly higher when catalyzed by surface-decorated Ir–Co/SiO<sub>2</sub> than by monometallic Ir/SiO<sub>2</sub>. Moreover, compared with Ir/SiO<sub>2</sub>, Ir–Co/SiO<sub>2</sub> has decreased 2-methylpentane selectivity but improved *n*-hexane selectivity. These catalytic behaviors were found to correlate with the surface-decorated bimetallic structure consisting of Co/SiO<sub>2</sub> decorated with surface Ir atoms.

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### 1. Introduction

The selective ring-opening (SRO) process of naphthenic compounds, during which only an endocyclic C-C bond is cleaved, leaving the number of carbon atoms in the reaction products unchanged, has great importance for improving the cetane number of diesel fuel.1-4 Numerous studies have shown good catalytic performance for SRO by using the noble metal catalysts (e.g. Ir, Pt, Ru, Rh).5-9 There are three main mechanisms10,11 for the ring-opening process of naphthenes catalyzed by noble metals: the dicarbene mechanism, multiplet mechanism and metallocyclobutane mechanism. When SRO reaction occurs according to the dicarbene mechanism, naphthenic compounds adsorb to the catalyst active sites perpendicularly via two carbon atoms of the naphthenic ring, which preferentially induces the breakage of C-C bond at the unsubstituted position of the ring.12,13 However, if the C-C bond is cleaved at the substituted position of the ring by the multiplet mechanism or the metallocyclobutane mechanism, the cetane number can be improved.10,14

Among the various noble metals, Ir is proven to be the most active and selective ring-opening catalyst, promoting the SRO

reaction of naphthenes through the dicarbene mechanism.<sup>15–19</sup> However, Ir is one of the rarest and most valuable elements on earth. Therefore, many attempts have been made to improve the catalytic performance of Ir and reduce the catalyst cost. González-Cortés *et al.*<sup>20</sup> reported a modified Ir-containing catalyst with the addition of potassium to improve the ring-opening selectivity for 1,3-dimethylcyclohexane. Shen *et al.*<sup>21</sup> synthesized bimetallic Pd–Ru catalyst for SRO of indane, which displayed the same high single-cleavage selectivity as Ir and was envisioned as a viable alternative to monometallic Ir.

Apart from the above methods, another desirable bimetallic catalyst structure, with active Ir atoms dispersed on the nanoparticle surfaces of the inexpensive metal (e.g. Co, Ni), will allow more Ir atoms to be exposed to the reactants and promote the SRO reaction. Ziaei-Azad et al.22 synthesized bimetallic coreshell structured nanoparticles with Ni atoms in the particle core and Ir atoms on the surface by hydrogen-sacrificial technique, and then loaded the nanoparticles onto the support for the SRO reaction of indane, significantly improving the catalytic activity compared to the monometallic Ir. As a model reaction, the SRO of MCP on supported metal catalysts has been extensively studied.23-25 Since ring opening of MCP on Ni catalyst is usually accompanied by extensive secondary cracking of the primary C<sub>6</sub>alkane hydrogenolysis products to C1-C5 paraffins,<sup>1</sup> in the current work, we selected Co nanoparticles to support the admetal Ir in order to avoid the excessive hydrogenolysis. Thus, the above leading works motivate us to explore surface-

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decorated Ir–Co bimetallic catalysts synthesized *via* a modified galvanic replacement,<sup>26,27</sup> an improved method based on the traditional impregnation method. Several characterization methods, including inductively coupled plasma atomic emission spectroscopy (ICP-AES), H<sub>2</sub>-temperature-programmed reduction (H<sub>2</sub>-TPR) and transmission electron microscopy (TEM), were employed to verify the structures and compositions of the catalysts and understand their catalytic behavior in the SRO reaction of MCP.

### 2. Experimental methods

#### 2.1. Catalyst preparation

The surface-decorated Ir-Co bimetallic catalysts were synthesized by a modified galvanic replacement in this study. The precursor Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in deionized water completely and then impregnated onto the SiO<sub>2</sub> support. After the impregnation process, the product was dried at 120 °C for 4 h and then calcined in air at 300 °C for 3 h to produce the calcined Co/SiO<sub>2</sub>. The calcined Co/SiO<sub>2</sub> was reduced by H<sub>2</sub>, cooled down to room temperature, and subsequently put into the aqueous solution of  $IrCl_3 \cdot xH_2O$  for continuous shaking. It should be pointed out that the reduced catalyst was put directly into IrCl<sub>3</sub>·xH<sub>2</sub>O solution, and the treatment of the reduced catalyst by flushing N2 to remove the adsorbed H2 has no obvious influence on the catalytic performance. Then, the supernatant was removed, and the resultant catalysts were washed and dried to obtain the surface-decorated bimetallic catalysts x%Ir-10%Co/SiO<sub>2</sub>, where x stands for the nominal weight ratio of Ir to the catalyst (x = 0.1, 0.3 and 1.0). The Co content of the bimetallic samples is 10 wt%, with the amount of metallic Co replaced by Ir being neglected.

For comparison, a traditional co-impregnation (CI) method was used to synthesize 1%Ir–10%Co/SiO<sub>2</sub>-CI catalyst. The precursors of IrCl<sub>3</sub>·*x*H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved in deionized water completely and impregnated onto the SiO<sub>2</sub> support. After the impregnation process, the catalyst was dried at 120 °C for 4 h and then calcined in air at 300 °C for 3 h to produce calcined 1%Ir–10%Co/SiO<sub>2</sub>-CI. The corresponding monometallic Ir/SiO<sub>2</sub> and Co/SiO<sub>2</sub> catalysts were also synthesized by impregnation method to serve as control samples.

#### 2.2. Catalyst characterization

2.2.1. Inductively coupled plasma atomic emission spectroscopy (ICP-AES). The concentration of  $Ir^{3+}$  during the galvanic replacement procedure was determined by ICP-AES. The experiments were carried out using a PerkinElmer Optima 7300V spectrometer with the radio-frequency power of 1300 W and plasma gas flow of 15 L min<sup>-1</sup>.

**2.2.2.** H<sub>2</sub>-temperature-programmed reduction (H<sub>2</sub>-TPR). TPR experiments were performed using a Micromeritics AutoChem II 2920 to determine the reduction behavior of the calcined catalysts. For each experiment, 0.10 g of calcined catalyst with 100–200 mesh was put into the U-shaped tubular quartz reactor. Then, the catalyst was exposed to the mixed gas consisting of 10.0 vol% H<sub>2</sub> in Ar with a temperature ramp from

room temperature to 700 °C at the rate of 10 °C min<sup>-1</sup>. A thermal conductivity detector (TCD) was used to detect the amount of hydrogen consumption. Furthermore, to compare the surface compositions of the catalyst, oxidation resistance experiments *via* a modified TPR process were performed. The catalysts were reduced, cooled down to room temperature, exposed to the air, and then used for the TPR experiment.

2.2.3. Transmission electron microscopy (TEM). TEM analysis was conducted on pre-reduced catalysts using a JEOL ARM 200F equipped with a cold-field emission gun operated at 200 keV and a Probe Cs corrector providing a point resolution of 0.8 Å at scanning transmission electron microscopy (STEM) mode. STEM imaging of bimetallic catalysts were measured on a JEOL ARM 200F equipped with a STEM-EDX (energydispersive X-ray spectroscopy) analysis system at a voltage of 200 kV. Spot size 4 with the spatial resolution of a few angstroms was used to obtain compositional line profile across the bimetallic catalysts. TEM samples were prepared by grinding and suspending reduced catalysts in ethanol, and then a few droplets of this solution were placed onto a carbon-coated copper grid. The samples were pretreated by ion cleaning and heating before being placed into the ARM 200F to obtain the atomic resolution images in STEM mode.

#### 2.3. Catalytic evaluation

Studies of SRO reaction for MCP were performed in a continuous flow, fixed-bed microreactor under 280 °C and 2.0 MPa. Before the reaction, 0.15 g of catalyst mixed with quartz powder was reduced by  $H_2$  at 350 °C (450 °C for monometallic Co/SiO<sub>2</sub>) for 1 h in the microreactor. Through the reduction process, the catalyst was completely reduced. During the reaction, the feedstock of MCP, with a liquid flow rate of 0.1 mL min<sup>-1</sup>, was carried to the reactor by a constant flow pump. The gas flow of  $H_2$  was 400 mL min<sup>-1</sup>. The products were analyzed by an online Agilent 7890 GC equipped with a flame ionization detector (FID).

### 3. Results and discussion

#### 3.1. Characterization of synthesis process by ICP-AES

During the synthesis of surface-decorated Ir–Co/SiO<sub>2</sub>, the different reduction potentials (1.16 V for the Ir<sup>3+</sup>/Ir pair and -0.28 V for the Co<sup>2+</sup>/Co pair) produce the driving force for the galvanic replacement reaction.<sup>28,29</sup> When reduced Co/SiO<sub>2</sub> was put into the Ir<sup>3+</sup> solution, it was assumed that a galvanic replacement reaction occurred between Ir<sup>3+</sup> and Co, leading to the preferential deposition of Ir on the surfaces of Co nanoparticles instead of SiO<sub>2</sub> support (Scheme 1). To verify the above assumption, the concentration of Ir<sup>3+</sup> before and after galvanic replacement during the synthesis procedure was measured (Table 1). Only trace amount of Ir<sup>3+</sup> (<15 mg L<sup>-1</sup>) remains in the supernatants after the galvanic replacement reaction, and the calculated loading ratio of Ir<sup>3+</sup> on the *x*%Ir–10%Co/SiO<sub>2</sub> catalyst is more than 90%, implying that most of the Ir<sup>3+</sup> in the aqueous precursor solution is loaded onto the catalyst.



Scheme 1 Illustration of the modified galvanic replacement from Co/SiO $_2$  to Ir–Co/SiO $_2$ .

Furthermore, a comparative experiment was performed to distinguish the distribution and state of the Ir species loaded onto the x%Ir-10%Co/SiO<sub>2</sub> catalyst, whether in the form of Ir<sup>3+</sup> via adsorption or metallic Ir via galvanic replacement reaction. The calcined 10% Co/SiO<sub>2</sub>, without the reduction process, was directly put into the aqueous precursor solution of IrCl<sub>3</sub>·xH<sub>2</sub>O with continuous shaking, then the supernatants were collected for ICP-AES analysis. The data in the second and last rows of Table 1 show little difference in Ir<sup>3+</sup> concentration between the supernatants and aqueous precursor solution, indicating that only trace amount of Ir<sup>3+</sup> is loaded onto the catalyst via adsorption. Therefore, it can be deduced that by the galvanic replacement reaction, most of the Ir<sup>3+</sup> in the aqueous precursor solution is preferentially deposited onto the surfaces of Co nanoparticles in the form of metallic Ir instead of Ir<sup>3+</sup> adsorbed by SiO<sub>2</sub> support.

#### 3.2. H<sub>2</sub>-TPR results

The reduction behavior of the calcined catalysts by TPR is shown in Fig. 1(a). The Co/SiO<sub>2</sub> shows two main reduction peaks at about 285 °C and 320 °C, which attribute to the successive reduction of Co<sub>3</sub>O<sub>4</sub> to CoO and CoO to metallic Co, respectively.<sup>30,31</sup> As shown in Fig. 1(a), Ir can be reduced at about 163 °C, lower than that of Co. Thus for Ir–Co/SiO<sub>2</sub>-CI, hydrogen that dissociates on the Ir surface could migrate to the surface of Co<sub>3</sub>O<sub>4</sub> and support, resulting in Co being reduced at much lower temperatures. These results also suggest that the catalysts were completely reduced by H<sub>2</sub> at 350 °C (450 °C for monometallic Co/SiO<sub>2</sub>).

To further verify the surface compositions of the catalysts, oxidation resistance experiments for the reduced catalysts were performed *via* a modified TPR process, the results of which are shown in Fig. 1(b). The  $H_2$ -TPR analysis of "Ir/SiO<sub>2</sub> (reduced-



Fig. 1 TPR profiles of (a) the calcined catalysts and (b) the "reducedoxidized" catalysts. The signal of 1%Ir/SiO<sub>2</sub> in (a) has been magnified 5 times. The "reduced-oxidized" catalysts were analyzed by a modified TPR process: the catalysts were reduced, cooled down to room temperature, exposed to the air, and then used for the TPR experiment.

oxidized)" shows an almost-flat profile, indicating that reduced Ir is nearly not oxidized in the air atmosphere at room temperature. For "10%Co/SiO<sub>2</sub> (reduced-oxidized)," the intense reduction peak around 180 °C can be attributed to the reduction of CoO, the oxidation state of Co at room temperature. Specially, for the three curves of "x%Ir–10%Co/SiO<sub>2</sub> (reduced-oxidized)" (x = 0.1, 0.3 and

Table 1       Ir <sup>3+</sup> concentration during the catalyst synthesis procedure							
Items	0.1%Ir <sup>a</sup>	0.3%Ir <sup>a</sup>	1%Ir <sup>a</sup>				
${ m Ir}^{3+}$ concentration in aqueous precursor solution (before galvanic replacement)/mg ${ m L}^{-1}$	55.7	167	562				
$Ir^{3+}$ concentration in the supernatants (after galvanic replacement) <sup>b</sup> /mg L <sup>-1</sup>	<1	14.5	14.2				
Loading ratio of $Ir^{3+}$ on the catalyst <sup>b</sup>	99.9%	91.3%	97.5%				
$Ir^{3+}$ concentration in the supernatants (comparative samples) <sup><math>c</math></sup> /mg L <sup><math>-1</math></sup>	32.0	154	569				

<sup>*a*</sup> For x%Ir (x = 0.1, 0.3 and 1), x stands for the nominal weight ratio of Ir to Ir–Co/SiO<sub>2</sub>. <sup>*b*</sup> Catalyst synthesis *via* the galvanic replacement reaction. <sup>*c*</sup> Comparative synthesis without the Co/SiO<sub>2</sub> reduction procedure.

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1.0), the intensity of reduction peaks for "CoO $\rightarrow$ Co" decreases compared to that for "10%Co/SiO<sub>2</sub> (reduced-oxidized)." These indicate that for the surface-decorated Ir–Co/SiO<sub>2</sub> catalysts, Ir atoms decorated on the surfaces of Co nanoparticles *via* galvanic replacement suppress the oxidation of Co at room temperature.

#### 3.3. TEM results

High-angle annular dark field (HAADF) TEM images and particle size distributions are shown in Fig. 2. Particle size distributions of the supported bimetallic nanoparticles, assuming a spherical shape, were obtained from the measurement of about 300 particles found in several arbitrarily chosen areas of enlarged micrographs. The dominant particle size in each catalyst appears to range in diameter from approximately 2 nm to 5 nm. The average diameter is 3.4, 3.2 and 2.9 nm for 0.3%Ir–10%Co/SiO<sub>2</sub>, 1%Ir–10%Co/SiO<sub>2</sub> and 1%Ir–10%Co/SiO<sub>2</sub>-CI, respectively.

Furthermore, STEM-EDX was used to measure the distributions of Ir and Co in the 1%Ir-10%Co/SiO<sub>2</sub> catalyst, as shown in Fig. 3. The images obtained by three scanning modes, including a selected point, selected line scan and selected area scan (Fig. 3(a-c)), show that all the bright nanoparticles are composed of Co atoms, while some brighter nanoparticles are composed of both Co and Ir atoms. Combining the STEM and HRTEM images (Fig. 3(d)), the distribution of Ir atoms is clearly identified as single atoms or clusters (<1 nm) situated at surfaces of Co nanoparticles.

#### 3.4. Catalytic evaluation

Flow reactor studies of SRO reaction for MCP were employed to compare the catalytic performance of different catalysts (Table 2). No detectable conversion of MCP is observed over monometallic Co/SiO<sub>2</sub>. For the monometallic Ir/SiO<sub>2</sub> catalysts, the increased Ir content from 0.1 wt% to 1 wt% gives a significant improvement of MCP conversion. On the other hand, for the surface-decorated x%Ir-10%Co/SiO<sub>2</sub>, with the increase of Ir content, the MCP conversion displays a volcano trend and reaches its maximum value at 0.3 wt%. It can be inferred that during the synthesis of x%Ir-10%Co/SiO<sub>2</sub>, the increased Ir<sup>3+</sup> concentration in aqueous precursor solution accelerates the reaction rate of galvanic replacement, leading to the nonuniform deposition of Ir atoms on the Co nanoparticle surfaces. Thus, the non-uniform deposition of Ir atoms restrains the catalytic behavior of 1%Ir-10%Co/SiO2. Moreover, Fig. 4 displays the mass-specific rate for SRO of MCP as a function of Ir content over monometallic Ir/SiO<sub>2</sub> and surfacedecorated bimetallic Ir-Co/SiO2. Increasing Ir content improves the mass-specific rate for monometallic Ir/SiO<sub>2</sub> but decreases it for Ir-Co/SiO<sub>2</sub> bimetallic catalysts. These suggest that SRO is sensitive to Ir content and the surface structure of bimetallic catalysts.

For 0.1 wt% and 0.3 wt% Ir content, MCP conversion (Table 2) and mass-specific rate of SRO (Fig. 4) are much higher when catalyzed by surface-decorated Ir–Co/SiO<sub>2</sub> than by monometallic Ir/SiO<sub>2</sub>. It could be explained that for Ir–Co/SiO<sub>2</sub>, the catalytically active Ir atoms are highly dispersed on the Co nanoparticle surfaces *via* the galvanic replacement reaction, thus significantly improving the dispersion and utilization of Ir compared to Ir/SiO<sub>2</sub>. A similar trend has also been observed on the SRO of indane over Ir–Ni bimetallic catalysts reported by Ziaei-Azad *et al.*<sup>22</sup> With the increase of Ir content to 1 wt%, the 1%Ir–10%Co/SiO<sub>2</sub> catalyst does not have an advantage



Fig. 2 TEM images and particle size distributions for (a) 0.3%Ir-10%Co/SiO<sub>2</sub>, (b) 1%Ir-10%Co/SiO<sub>2</sub> and (c) 1%Ir-10%Co/SiO<sub>2</sub>-CI.



Fig. 3 Representative STEM images in (a) a selected point, (b) selected line scan mode, (c) selected area scan mode (mapping), and (d) HRTEM images of 1%Ir-10%Co/SiO<sub>2</sub> catalyst. The green signals stand for Co and blue signals for Ir in (b) and (c).

compared to 1%Ir/SiO<sub>2</sub>. At the same time, compared with another two catalysts with 1 wt% Ir (1%Ir-10%Co/SiO<sub>2</sub> and 1%Ir/SiO<sub>2</sub>), 1%Ir-10%Co/SiO<sub>2</sub>-CI shows the least catalytic activity for SRO of MCP. The content of Co in 1%Ir-10%Co/SiO<sub>2</sub>-CI is much higher than that of Ir, with the Co/Ir atomic ratio of 33 : 1. Therefore, one possible reason is that most Ir atoms in 1%Ir-10%Co/SiO<sub>2</sub>-CI are covered by Co atoms through the co-

impregnation synthesis procedure and not exposed on the catalyst surfaces.

The SRO reaction of MCP produces *n*-hexane (*n*-H), 2-methylpentane (2MP) and 3-methylpentane (3MP) (Scheme 2). Previous research studies have demonstrated that SRO reaction occurs according to a multiplet mechanism, a dicarbene

catalysts <sup>a</sup>									
	- ·	RO selectivity <sup><math>b</math></sup> (%)							
Catalysts	Conversion (%)	SUM	2MP	3MP	n-H	2MP/3MP			
0.1%Ir/SiO <sub>2</sub>	2.8	99.8	70.5	28.9	0.4	2.4			
0.1%Ir-10%Co/SiO <sub>2</sub>	18.3	77.2	46.0	28.1	3.1	1.6			
0.3%Ir/SiO <sub>2</sub>	10.5	98.6	70.3	28.1	0.2	2.5			
0.3%Ir-10%Co/SiO <sub>2</sub>	21.9	76.9	46.8	27.1	3.0	1.7			
1%Ir/SiO <sub>2</sub>	75.0	99.1	71.7	27.1	0.3	2.6			
1%Ir-10%Co/SiO <sub>2</sub>	12.7	79.8	47.8	28.8	3.2	1.7			
1%Ir-10%Co/SiO <sub>2</sub> -CI	0.4	100	69.0	29.5	1.5	2.3			
10%Co/SiO <sub>2</sub>	0		—		—	_			

Table 2 Catalytic performance of Ir-Co bimetallic and monometallic

<sup>*a*</sup> Reaction conditions: catalyst 0.15 g, pressure 2.0 MPa, temperature 280 °C. <sup>*b*</sup> 2MP: 2-methylpentane; 3MP: 3-methylpentane; *n*-H: *n*-hexane; SUM: the sum of 2MP, 3MP and *n*-H.



Fig. 4 Mass-specific rate as a function of Ir content for monometallic  $Ir/SiO_2$  and surface decorated bimetallic  $Ir-Co/SiO_2$ .



Scheme 2 Ring-opening products of MCP.

mechanism and a metallocyclobutane mechanism over different noble metals.<sup>1,10,11,32</sup> The multiplet mechanism is usually observed over Pt catalysts, with an equal probability of breaking endocyclic bonds, producing the statistical ratio of  $2MP: 3MP: n-H = 2: 1: 2.^{10,33}$  The dicarbene mechanism often happens over Ir catalysts, which preferentially induces endocyclic C–C bond breakage at the unsubstituted position of the ring, leading to the statistical ratio of 2MP: 3MP = 2: 1 and trace amounts of *n*-H.<sup>12,13</sup> In addition to these two typical mechanisms for SRO reaction, Gault *et al.*<sup>34,35</sup> proposed an alternative one that would operate through a metallocyclobutane intermediate consisting of a metal atom and three C atoms, which would allow the breakage of substituted C–C bonds if an external methyl group were involved in the intermediate.

The ring-opening (RO) selectivity, product distribution and molar ratio of 2MP/3MP are listed in Table 2. The results of Ir/ SiO<sub>2</sub> in the present work are consistent with previous research work showing that the hydrogenolysis of MCP over Ir-based catalysts is selective to the formation of 2MP and 3MP.<sup>1,17</sup> More interestingly, the surface-decorated Ir-Co/SiO<sub>2</sub> and monometallic Ir/SiO<sub>2</sub> show quite different behaviors in terms of product selectivity. The RO selectivity over Ir-Co/SiO<sub>2</sub> is about 76-80%, lower than the 99% over Ir/SiO<sub>2</sub>. The cracking products on Ir-Co/SiO<sub>2</sub> mainly include methane, butane and 2-methylbutane, as analysed by gas chromatography-mass spectrometry (GC-MS). Meanwhile, compared with Ir/SiO<sub>2</sub>, Ir-Co/SiO<sub>2</sub> shows a lower selectivity toward 2MP (~47% vs. 71%), corresponding to lower 2MP/3MP ratio (~1.6 vs. 2.5) but higher selectivity toward *n*-H ( $\sim$ 3.1% vs. 0.3%). Therefore, it can be inferred that the SRO reaction of MCP over Ir-Co/SiO<sub>2</sub> follows a different mechanism compared to monometallic Ir/SiO<sub>2</sub>.

As reported by Chen and other research groups,<sup>36-40</sup> bimetallic catalysts often show electronic and chemical properties that differ distinctly from those of the parent metals. For example, it has been demonstrated that Pt-terminated Pt-Co-Pt(111) surface, which represents a subsurface bimetallic structure with Pt on the top-most surface layer and Co residing in the subsurface region, shows much higher activity for the hydrogenation of cyclohexene than Co-terminated Co-Pt-Pt(111) and the corresponding monometallic surfaces.<sup>41</sup> The catalytic hydrogenation pathway on the subsurface bimetallic structures has been correlated to the modification of the electronic properties of Pt by the subsurface Co atoms.42 It is possible that such effect also plays a role in the SRO reaction of MCP over the surface-decorated Ir-Co/SiO<sub>2</sub> bimetallic catalysts. Moreover, X-ray photoelectron spectroscopy (XPS) should shed light on the electronic effects of surface-decorated structure. However, at the lower Ir content, the overlapping of Ir 4f and Co

3p levels makes it very difficult to determine the exact binding energy shift.<sup>43</sup> More detailed density functional theory (DFT) calculations would be needed to further understand the electronic properties.

### 4. Conclusions

We explored the utilization of surface-decorated Ir-Co bimetallic catalysts synthesized via galvanic replacement for the selective ring-opening of MCP. Results from ICP-AES show that by the galvanic replacement reaction, most of the Ir<sup>3+</sup> in the precursor solution is preferentially deposited onto the surfaces of Co nanoparticles in the form of metallic Ir instead of Ir<sup>3+</sup> adsorbed by SiO<sub>2</sub> support. The modified TPR results show that Ir atoms decorated on the surfaces of Co nanoparticles via galvanic replacement suppress the oxidation of Co at room temperature. TEM measurements provide additional information on the metallic particle size distribution, and the combination of STEM-EDX and HRTEM images identifies the single atoms or clusters of Ir situated at the surface of Co nanoparticles. At optimized Ir content, MCP conversion and massspecific rate of SRO are significantly higher when catalyzed by surface-decorated Ir-Co/SiO<sub>2</sub> than by monometallic Ir/SiO<sub>2</sub>. Moreover, compared with Ir/SiO2, Ir-Co/SiO2 decreases 2-methylpentane selectivity but improves the n-hexane selectivity, which is attributed to the surface-decorated bimetallic structure consisting of Co/SiO<sub>2</sub> decorated with surface Ir atoms. Results from the current study also identify research opportunities in synthesizing supported bimetallic catalysts by surface decoration via galvanic replacement.

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