RuO$_2$ supported NaY zeolite catalysts: Effect of preparation methods on catalytic performance during aerobic oxidation of benzyl alcohol

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1. Introduction

The typical structure of heterogeneous catalysts consists of an active metal phase supported on a nanoporous support (or carrier), often promoted by the addition of alkali or alkali-earth metals [1,2]. The active metal phase is generally in the form of nanoparticles, which can be rigidly bound on the supporting materials; these supports are generally nanoporous architectures with high surface areas and pore volumes. Zeolites are among the most widely used nanoporous supports. Zeolites are crystalline microporous materials with a framework consisting of a regular arrangement of silicon and/or aluminum species that are tetrahedrally coordinated by four oxygen atoms [3–8]. The uniform micropores of zeolites are very useful for achieving size/shape-selective catalysis depending on the reactant molecules [7,8]. In addition, zeolites can be used as catalyst supports for accommodation of metal nanoparticles within the micropores or outside the zeolite framework due to their high surface area. Various synthesis methods for the construction of such zeolite-supported metal nanoparticle catalysts have been developed [9–18]. For example, metal precursors have been impregnated into the micropores of zeolites, followed by treatment with oxygen (oxidation) or hydrogen (reduction) [9–12]. This technique is termed the impregnation method, and is widely used to introduce designated amounts of metal precursors into the zeolite micropores. As another method, metal cations can also be introduced into the zeolite framework by post ion-exchange by exploiting the ion-exchange ability of the aluminosilicate...
component of the zeolite framework [12–15]. Because the ion-exchange technique utilizes the ion-exchange sites on the zeolite framework, the metal cation loading is determined by the number of ion-exchange sites. Simultaneous crystallization of the zeolite framework under hydrothermal conditions in the presence of metal precursors has also been utilized to achieve uniform dispersion of the metal nanoparticles within the zeolite micropores [16–18].

Despite the variety of synthetic procedures for fabricating efficient zeolite-supported metal nanoparticles, no comparative study of the detailed differences between the preparation methods has been documented to date. In the present work, a comprehensive comparative catalytic study of the effect of various preparation methods on the catalytic consequences during the aerobic oxidation of benzyl alcohol is presented. This is an important catalytic process for the production of chemical intermediates and fine chemicals as the major product (i.e., benzaldehyde) is known as the second most important aromatic flavor molecule (after vanillin) used in the cosmetics industry [19–21]. Among the various metal nanoparticle-based heterogeneous catalysts, RuO2 is selected for the construction of RuO2 supported zeolite catalysts and NaY zeolite is selected as the catalyst support based on its ability to provide large pores comprising 12-membered-rings and its high concentration of ion-exchange sites. Simultaneous crystallization of the zeolite framework in the presence of RuCl3 under hydrothermal synthetic conditions, (ii) post ion-exchange with an aqueous solution containing RuCl3 on a NaY zeolite framework, and (iii) post support of preformed Ru metal nanoparticles with an average diameter of 2.5 nm onto the zeolite surface; the samples are denoted as Ru(SC)/NaY, Ru(IE)/NaY, and Ru(PS)/NaY, respectively. The catalytic consequences of these catalysts are investigated during the aerobic oxidation of benzyl alcohol to benzaldehyde under liquid-phase conditions as functions of the reaction time and temperature. The results show dramatic differences in the activity, rate constant, activation energy, and recyclability depending on the pathway selected for catalyst preparation.

2. Material and methods

2.1. Chemicals

The following chemicals were used in this study: NaOH (Daejung; ≥97.0%), polyvinylpyrrolidone (PVP, Sigma-Aldrich; Mn ≥ 55,000), ethylene glycol (Sigma-Aldrich; ≥99.0%), RuCl3 (Sigma-Aldrich; Ru content 45–55%), NaAlO2 (Sigma Aldrich; 53 wt% Na2O, 42.5 wt% Al2O3), water glass (Daejung; 29 wt% SiO2, 9.5 wt% Na2O in H2O). All chemicals were used without any further purification.

2.2. Synthesis of RuO2 supported NaY zeolites

2.2.1. Synthesis of NaY zeolite

For synthesis of the NaY zeolite, two synthesis gels were separately prepared in polypropylene bottles following the literature reported elsewhere [22]. One was a seed gel, and the other was a feedstock gel. For preparation of the seed gel, NaAlO2 (as an alumina precursor) was mixed with NaOH in water and stirred until dissolved. Subsequently, water glass (as a silica precursor) was added to give a final seed gel composition of 0.53 Na2O/0.05 Al2O3/0.5 SiO2/0.1 H2O. The feedstock gel was prepared by mixing NaAlO2 with NaOH in water with stirring until the solids dissolved. Subsequently, water glass was added to give a final feedstock gel composition of 4.09 Na2O/0.95 Al2O3/9.5 SiO2/171 H2O. The resultant seed and feedstock gels were further aged at room temperature for 1 d under stirring. The seed gel was then added to the feedstock gel at once and the resultant final gel was shaken vigorously for homogenization. After additional aging at room temperature for 5 h under stirring, the gel was hydrothermally aged for 12 h in a Teflon-lined autoclave in an oven at 100 °C under static conditions. During the hydrothermal treatment, a white solid precipitate was gradually formed at the bottom of the polypropylene bottle, and was collected by filtration using a funnel filter, washed with deionized water to remove the water-soluble chemical residues, and dried in an oven at 120 °C. The final product was NaY.

2.2.2. Preparation of Ru(SC)/NaY

The overall procedure for synthesis of the Ru(SC)/NaY sample was adopted from the synthesis of NaY described above, wherein RuCl3 was mixed with the synthesis gel as an additional step. In a detailed synthesis, 0.515 g of RuCl3 was added to the final gel obtained after mixing the feedstock gel with the seed gel. This final synthesis gel containing RuCl3 was further homogenized by stirring for 5 h and then hydrothermally treated for 12 h in a Teflon-lined autoclave in an oven at 100 °C under static conditions. The final product was collected by the same procedure described above, which gave the final product (i.e., Ru(SC)/NaY).

2.2.3. Preparation of Ru(IE)/NaY

For the preparation of the Ru(IE)/NaY sample, 1 g of the NaY zeolite synthesized as described above was mixed with 10 mL of aqueous solution containing RuCl3 (0.103 M) to produce Ru(III)-exchanged NaY zeolite. The solution mixture was further stirred for 24 h in a polypropylene bottle at room temperature; the product was collected by filtration, washed with deionized water, and dried in an oven at 120 °C. Subsequently, the zeolite product was calcined at 300 °C for 3 h under flowing O2 at 50 cm3 min−1, which gave the final product (i.e., Ru(IE)/NaY).

2.2.4. Preparation of Ru(PS)/NaY

For preparation of the Ru(PS)/NaY sample, Ru metal nanoparticles capped with polyvinylpropylene (PVP) were firstly prepared in a different synthesis batch. NaOH (200 mg) and PVP (585 mg) were dissolved in 10 mL of ethylene glycol and then added to 10 mL of an ethylene glycol solution containing 80 mg of RuCl3 in a 50 mL two-neck round-bottom flask equipped with a reflux condenser. The solution was stirred for 30 min under vacuum. The flask was evacuated and refilled with N2 via a Schlenk line. This solution was heated to 160 °C in an oil bath under N2 atmosphere and stirred for 3 h. After the solution cooled to room temperature, the Ru nanoparticles were collected by centrifugation at 8000 rpm for 20 min, washed with acetone, and re-dispersed in ethanol to give an approximate concentration of 2 mg mL−1. A 5 mL aliquot of this solution was mixed with 1 g of NaY zeolite in a conical tube, which was sonicated for 1 h at room temperature to support the Ru metal nanoparticles on the surface of the NaY zeolite. After dispersion of the Ru metal nanoparticles on the NaY zeolite, the final sample was collected by centrifugation and dried in an oven at 120 °C. The dried sample was calcined at 300 °C for 3 h under flowing O2 at 50 cm3 min−1, which gave the final product (i.e., Ru(PS)/NaY).

2.3. Characterization

X-ray diffraction (XRD) patterns were acquired with a Rigaku X-ray diffractometer using Cu-Kα radiation (λ = 0.1541 nm) at 40 kV and 40 mA. The content of Ru in the catalysts was analyzed by using inductively-coupled plasma atomic emission spectroscopy (ICP-AES). The CO chemisorption of catalysts were measured with a BELCAT apparatus (MicrotracBel, Japan). Prior to the measurement,
catalysts were pre-treated by heating at 300 °C with 10% H₂ and 90% He gas mixture. The Ru dispersion was calculated using CO pulse chemisorption measurements with 10% CO and 90% He gas flow at 50 °C.

2.4. Aerobic oxidation of benzyl alcohol

In a typical experiment, 0.1 g of catalyst was added to 20 mL of toluene containing 0.208 mL of benzyl alcohol and 0.195 mL of decane as an internal standard in a 50 mL two-neck flask equipped with a reflux condenser. The reaction solution was heated to temperatures in the range of 35–70 °C while supplying O₂ at a flow rate of 20 cm³ min⁻¹, controlled by a flow-meter. During the catalytic reaction, a small aliquot of the reaction solution was collected periodically to analyze the product by using gas chromatography (YL6500) equipped with a flame-ionization detector (FID) and a capillary column (DB-5, 30 m length, 0.32 mm i.d., 1.5 μm thickness). The conversion of benzyl alcohol was calculated based on the internal standard, and benzaldehyde was the major product without other detectable amounts of byproducts.

3. Results and discussion

Fig. 1 shows the powder XRD patterns of the zeolite catalysts prepared in this work. For comparison, the profile of NaY zeolite without supporting Ru is presented as a reference (black color). The XRD patterns of the three different catalysts in the as-synthesized forms without calcination (blue colors) were compared with those of the samples calcined after thermal treatment under flowing oxygen (red colors) and with those of the spent catalysts after the 1st catalytic run and subsequent re-calcination under flowing oxygen (green colors). For the as-synthesized catalysts, the overall XRD patterns were similar to the reference pattern of NaY zeolite (black). Only the intensity and broadness of the XRD peaks differed depending on the preparation methods and the presence of Ru metal. Among the three catalysts, the Ru(SC)/NaY catalyst gave rise to the most intense XRD peaks for the as-synthesized and calcined forms (Fig. 1(a–b)), whereas the profiles of the other two catalysts showed less intense XRD peaks.

Thermal treatment under an oxygen flow can oxidize the Ru metal or ions to RuO₂ phases. Indeed, after calcination at 300 °C under an oxygen flow, new XRD peaks appeared at 20 values of 28 and 35° (red asterisks in Fig. 1). These XRD peaks correspond to the (110) and (101) reflections of the crystalline RuO₂ phase [23]. The intensities of the peaks at 20 values of 28 and 35° differed according to the catalyst. The intensity of the peak at 35° decreased in the order: Ru(IE)/NaY, Ru(SC)/NaY, and Ru(PS)/NaY, as shown in Fig. 1(c), (b), and (h), respectively. These differences could be attributed to the different degrees of oxidation or the different sizes of the individual RuO₂ nanoparticles.

The catalytic performance of the RuO₂ metal supported zeolite catalysts (i.e., Ru(SC)/NaY, Ru(IE)/NaY, and Ru(PS)/NaY) was investigated in the aerobic oxidation of benzyl alcohol. Table 1 summarizes the reaction results, highlighting the conversion of benzyl alcohol as a function of the reaction temperature and the corresponding turnover frequency (TOF) values based on the number of exposed catalytic sites, calculated from CO chemisorption analysis. No conversion of benzyl alcohol occurred in the absence of the catalyst and oxidant (Entry 1 in Table 1), and the major product was benzaldehyde without appreciable FID peaks for other products such as benzoic acid and benzene benzoate based on GC analyses. The conversion of benzyl alcohol increased gradually when the reaction temperature increased from 35 to 50 and 70 °C (Entries 2–10 in Table 1). However, no significant differences in the conversion were observed for the three catalysts, where the conversion was generally in the range of 8–13% in the given reaction time of 3 h. Nonetheless, the TOF values varied drastically. The Ru(PS)/NaY catalyst had significantly higher TOF values, within the range of 33–48 h⁻¹, whereas the other catalysts exhibited much smaller values of 9–12 h⁻¹ depending on the reaction temperature. The markedly higher TOF value of Ru(PS)/NaY might be attributed to the much stronger catalytic action of the individual RuO₂ sites relative to that of the other two catalysts. Alternatively, the RuO₂ metal nanoparticles in the Ru(PS)/NaY catalyst are more easily accessible to the reactants than those in the Ru(SC)/NaY and Ru(IE)/NaY catalytic systems. Because the preformed RuO₂ metal nanoparticles with an average diameter of 2.5 nm could not enter the micropore aperture (ca. 0.7 nm) of NaY, they are thought to be supported mostly on the external surface of the NaY zeolite. This may facilitate collision of the reactant with the active sites on the metal nanoparticles.

Fig. 2(A) shows the kinetic profiles of the three catalysts. The change in the normalized concentration (C/C₀) of benzyl alcohol is shown as functions of the reaction times (t) and temperatures, where C₀ is the initial concentration of benzyl alcohol and C is the concentration of benzyl alcohol at time t. The catalytic aerobic oxidation of benzyl alcohol was also fitted to a 1st order kinetic model by plotting ln(C/C₀) versus time (t) in Fig. 2(B). A good linear regression with correlation coefficients (R²) of >0.9941 (Table 2) was obtained, which is in good agreement with the 1st order
reaction kinetics reported elsewhere [24–26]. The 1st-order rate constants \( k_1 \) could be obtained from the slopes of the regression lines. As summarized in Table 2, the rate constant increased as the temperature increased. The rate constant of the Ru(SC)/NaY catalyst changed most dramatically as the reaction temperature increased from 35 to 50 and 70 °C. The rate constant of Ru(SC)/NaY at 35 °C was the smallest at 0.0030 h\(^{-1}\), but this catalyst had the largest rate constant of 0.0209 h\(^{-1}\) at 70 °C. In the case of the Ru(IE)/NaY catalyst, the rate constant changed from 0.0068 h\(^{-1}\) to 0.0176 h\(^{-1}\) as the reaction temperature changed from 35 °C to 70 °C. In the case of the Ru(SC)/NaY catalyst, only a marginal increase in the rate constant was observed upon increasing the reaction temperature.

According to the Arrhenius equation, the rate constant \( k_1 \) is related to the activation energy \( E_a \) as \( k_1 = A \exp(-E_a/RT) \), where the

### Table 1
Characterization of the catalysts and the reaction results for aerobic oxidation of benzyl alcohol to benzaldehyde.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Ru content (wt%)</th>
<th>CO chemisorption result</th>
<th>Temperature (°C)</th>
<th>BzOH conversion (%)</th>
<th>TOF (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>blank</td>
<td>none</td>
<td>none</td>
<td>35</td>
<td>0</td>
<td>–</td>
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<tr>
<td>2</td>
<td>Ru(SC)/NaY</td>
<td>9.2</td>
<td>7.5</td>
<td>35</td>
<td>9.42</td>
<td>9.20</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>10.73</td>
<td>10.47</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td>70</td>
<td>12.25</td>
<td>11.96</td>
</tr>
<tr>
<td>5</td>
<td>Ru(IE)/NaY</td>
<td>2.6</td>
<td>26.9</td>
<td>35</td>
<td>10.06</td>
<td>9.68</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>11.27</td>
<td>10.85</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td>70</td>
<td>12.35</td>
<td>11.89</td>
</tr>
<tr>
<td>8</td>
<td>Ru(PS)/NaY</td>
<td>1.6</td>
<td>10.4</td>
<td>35</td>
<td>8.20</td>
<td>33.19</td>
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<td>9</td>
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<td>50</td>
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<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>70</td>
<td>13.13</td>
<td>47.83</td>
</tr>
</tbody>
</table>

\( ^a \) Ru content obtained by ICP-AES.

\( ^b \) Conversion calculated at 3 h.

\( ^c \) Turnover frequency (TOF) calculated at 3 h conversion based on the total number of exposed Ru atoms, calculated from CO chemisorption.

### Table 2
Linear regression results of 1st order kinetics and Arrhenius plots for the aerobic oxidation of benzyl alcohol to benzaldehyde.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. (°C)</th>
<th>1st-order kinetic parameters</th>
<th>Arrhenius plot parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( y = ax + b )</td>
<td>( y = \frac{m}{h}x + n )</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0072x - 0.0060</td>
<td>0.0072</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.0105x - 0.0142</td>
<td>0.0105</td>
</tr>
<tr>
<td>Ru(IE)/NaY</td>
<td>35</td>
<td>0.0068x - 0.0004</td>
<td>0.0068</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0089x - 0.0077</td>
<td>0.0089</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.0176x - 0.0069</td>
<td>0.0176</td>
</tr>
<tr>
<td>Ru(PS)/NaY</td>
<td>35</td>
<td>0.0030x - 0.0093</td>
<td>0.0030</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0090x - 0.0111</td>
<td>0.0090</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.0209x - 0.0044</td>
<td>0.0209</td>
</tr>
</tbody>
</table>
values of $A$ and $E_a$ can be determined from the slope and y-intercept of the linear plot of $\ln k_1$ versus $1/T$. Arrhenius plots were constructed by using the rate constants at the three different reaction temperatures (derived above). As shown in Fig. 2(C), very good linear regressions of the Arrhenius plots obtained, with correlation coefficients ($R^2$) in the range of 0.9629–0.9982 (Table 2). The activation energy ($E_a$) and the pre-exponential factor ($A$) were respectively derived from the slope and y-intercept. The activation energy decreased in the order: Ru(PS)/NaY, Ru(IE)/NaY, and Ru(SC)/NaY with respective values of 48.39, 24.11, and 18.58 kJ mol$^{-1}$. Notably, these $E_a$ values are much lower than the bond dissociation energies of O-H (460 kJ mol$^{-1}$) in benzyl alcohol and molecular oxygen (498 kJ mol$^{-1}$) [27], which is indicative of the catalytic effects of RuO$_2$ in the zeolite catalysts on the oxidation of benzyl alcohol in the presence of molecular oxygen. The pre-exponential factor, a mathematical constant that could also be physically defined as the collision frequency factor, was $5.22 \times 10^{12}$ h$^{-1}$ for the Ru(PS)/NaY catalyst, which is about 5 orders of magnitude larger than that of the Ru(SC)/NaY catalyst ($7.15 \times 10^{11}$ h$^{-1}$). This suggests that the Ru(PS)/NaY catalyst enhances the frequency of collisions between benzyl alcohol and molecular oxygen, which explains the higher catalytic activity (i.e., TOF value) of the Ru(PS)/NaY catalyst relative to those of the Ru(SC)/NaY and Ru(IE)/NaY catalysts in spite of the higher $E_a$ value of the former.

The recyclability of the three catalysts was investigated under the same reaction conditions (Fig. 3). For the recyclability test, the catalysts were separated from the reaction mixture and reused under the same catalytic conditions after re-calcination under an oxygen flow to regenerate the RuO$_2$ phase; the change in the crystallinity of the catalyst after the reaction and the regeneration of the RuO$_2$ phase were analyzed via XRD. As shown in Fig. 1, no significant change in the XRD patterns corresponding to the NaY zeolite framework were observed (green colors) as compared to the fresh catalysts after calcination (red colors), indicating that the crystallinity of the zeolite was almost fully retained without significant collapse after the 1st run. However, the XRD reflections corresponding to the RuO$_2$ phase changed depending on the catalysts. The most significant change in the XRD reflections of the RuO$_2$ phase were observed for the Ru(IE)/NaY catalyst, wherein the XRD reflections at 28 and 35$^\circ$ almost completely disappeared after the 1st catalytic run and subsequent calcination in oxygen flow (Fig. 1(f)). When this Ru(IE)/NaY catalyst was tested in five repetitive catalytic runs, the initial activity for conversion of benzyl alcohol in a given reaction time (24 h) decreased significantly from 38.21% for the 1st run to 11.19% for the 5th run. This is consistent with the disappearance of the peaks of the RuO$_2$ phase in the XRD patterns. Considering that the XRD reflections of the RuO$_2$ phase disappeared, it can be deduced that preservation of the RuO$_2$ phase is important for sustainable catalytic performance.

In the case of Ru(PS)/NaY, the activity increased in the 2nd run (52.48%) relative to the initial activity (42.12%), but decreased to 15.26% in the 5th run. The increase in the catalytic activity in the 2nd run might be attributed to the removal of the PVP capping agent on the RuO$_2$ nanoparticles. Although the PVP capping agent should be removed upon thermal treatment under the oxygen flow at 300 °C, this temperature is not sufficiently high to remove all of the organic species in the catalyst. Therefore, during the 1st catalytic run and subsequent re-calcination at 300 °C, some residual PVP might be removed, and hence, the exposed surface area of the RuO$_2$ nanoparticles could be increased. This may be responsible for the increased catalytic activity in the 2nd run. This is also supported by the XRD patterns, in which the reflections corresponding to the RuO$_2$ phase were maintained after the 1st run (green asterisks in Fig. 1(b)). As expected, this catalyst exhibited the best recyclability, where the initial catalytic activity was maintained without significant deactivation during the five catalytic runs. As compared to other preparation methods, the simultaneous crystallization of the NaY zeolite in the presence of RuCl$_3$ precursors leads to the stable formation of RuO$_2$ metal nanoparticles confined within the micropore spaces. This may help to preserve the initial structure of the RuO$_2$ metal nanoparticles, which eventually enables better recyclability relative to the other catalysts.

4. Conclusions

Thus far, various synthesis procedures have been reported for the design of RuO$_2$-supported NaY zeolite catalysts. In this study, three representative preparation methods were adopted for construction of three different catalyst systems. Three types of RuO$_2$-supported NaY zeolite catalysts were prepared via (i) simultaneous crystallization of the zeolite framework in the presence of RuCl$_3$, (ii) post ion-exchange with RuCl$_3$ on the zeolite framework, and (iii) post support of preformed Ru metal nanoparticles on the zeolite surface, which respectively led to the construction of Ru(SC)/NaY, Ru(IE)/NaY, and Ru(PS)/NaY. From catalytic studies of the aerobic oxidation of benzyl alcohol, we reveal that the preparation methods can remarkably influence the catalytic consequences in terms of the site-based activity (TOF), activation energy ($E_a$), collision frequency factor ($A$), and recyclability. Although the level of benzyl alcohol conversion was within a similar range with the use of all three catalysts, the TOF and the calculated $E_a$ values differed. Among the three catalysts, the RuO$_2$ nanoparticles supported on the external surface of NaY zeolite crystals enhanced the frequency of collision between the reactants and the catalyst; thus, the Ru(PS)/NaY catalyst showed the highest TOF in spite of having the highest $E_a$. Relative to the Ru(PS)/NaY catalyst, no significant differences in the catalytic activity were observed for the Ru(SC)/NaY and Ru(IE)/NaY catalysts. However, among the three catalysts, the Ru(SC)/NaY catalyst showed much better recyclability. This catalyst exhibited sustainable activity without significant loss of the initial activity during five repetitive runs, as elucidated by XRD analysis, where the RuO$_2$ phase was almost fully preserved during repetitive catalytic reactions. The present comparative study provides information for the design of catalysts with better catalytic performance.

Fig. 3. Recyclability tests of Ru(SC)/NaY, Ru(IE)/NaY and Ru(PS)/NaY catalysts.
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