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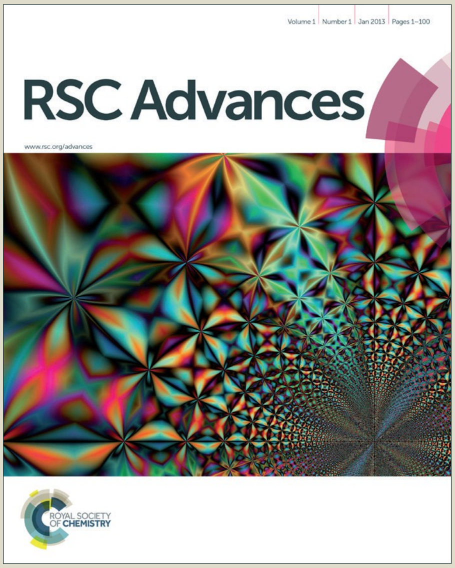

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ARTICLE

# Preparing acid-resistant Ru-based catalysts by carbothermal reduction for hydrogenation of itaconic acid

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Catalytic conversion and application of bio-based platform chemicals is of great significance. Itaconic acid, one of abundant and renewable bio-based platform chemicals, could be hydrogenated to produce methylsuccinic acid, which has important prospects in pharmaceutical synthesis. Traditional catalysts run the risks of being corroded, leached and deactivated acid reaction environment, and the stability of catalysts meets great challenge. Carbothermal reduction was employed t prepare stable ruthenium-based catalysts, and results confirmed that CO generated in situ functioned as an efficient reducing species in carbothermal reduction process. The catalysts were applied for hydrogenation of itaconic acid, which showed good stability and resistance to acid with no obvious loss of activity and less leaching in recycling tests compared to hydrogen reduced samples which exhibited apparent decrease of 22% in conversion of itaconic acid. Carbothermal reduced catalysts could remain 99% conversion and 99% selectivity of methylsuccinic acid, and maintained good stability and acid-resistance in higher temperature and longer reaction time.

## Introduction

Itaconic acid, one of abundant bio-based platform chemicals, is an important renewable unsaturated organic acid that can be easily obtained by fermentation of biomass-derived carbohydrates.[1, 2] It has great potentials as a key substrate to produce methylsuccinic acid through hydrogenation, which has chirality and extensive applications in organic synthesis especially for pharmaceutical synthesis.[3, 4]

Direct hydrogenation of unsaturated organic acids to produce saturated carboxylic acids is a much essential and significant reaction, which has been studied extensively.[1, 5] Homogeneous metal catalysts are widely applied affording good catalytic performance.[6] However, costs of metal complexes and challenge to be recovered and reused, make it difficult to meet the needs of application. While using heterogeneous metal catalysts could be alternative for avoiding these problems.[7-9] Nevertheless, there is an important issue that the stability of catalysts is hard to guarantee in the acid reaction environment. This may be resulted from acid corroding and leaching of active component, which leads to deactivation of catalysts.[10, 11] Developing stable heterogeneous catalytic systems with good resistance to acid has gained lots of attentions and became a key issue for direct hydrogenation of organic acids. Liu et al prepared silica-supported Pt complex for hydrogenation of itaconic acid, which showed about 90% of product yields. The yields were affected by the number of used times and decreased by 9% in the fourth time.[12] Catalysts Rh-BPPM and Ru-BINAP heterogenised on hexagonal mesoporous silicas were prepared for hydrogenation of itaconic acid in Jamis's work. The catalysts showed more than 10% loss of activity in three recycling times.[13, 14] This trend of catalyst activity during recovery and reuse is consistent with that observed in numbers of reports.[15-17] It is notable and essential to develop heterogeneous catalysts with good acid-resistance for hydrogenation of organic acid.

Carbothermal reduction provides an opportunity of novel potential methods for preparing highly efficient and stable catalysts in recent reports.[18-20] Catalysts prepared by this method have an uniform dispersion of nanoparticles, which resulting in higher catalytic activity.[21-23] More importantly, the stability of these catalysts is studied with remarkable results of recycling tests such as negligible loss of activity, ignorable leaching and lack of aggregation.[24] Su et al prepared Ru catalysts supported on carbon substrates by thermal reduction method, and these highly active catalysts showed good stabilities for the hydrogenation of monoaromatic.[25, 26] The carbothermal reduction process is complex and has mu importance with the reduction of metal species, the interaction between metal and supports, the stability and so on. A further research of this process could help to a better understanding of carbothermal reduction with its influence. In the work of Su et al, it was observed that carbon species played a vital role in the reduction and formation of Ru-carbo contact in the reduction process, which may anchor ar

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Electronic Supplementary Information (ESI) available: Details of the synthesis and characterization of the materials and calculation methods of experiments. See DOI: 10.1039/x0xx00000x immobilize the Ru particles.[26] Yang et al prepared cobalt-based catalysts via carbothermal reduction, and they proposed that the diffused oxygen atoms could react with the carbon supports yielding CO. [27, 28]We had prepared Ni/AC catalysts with carbothermal reduction method and applied in the hydrogenolysis of lignin model compound. We considered that nickel nitrate was decomposed and then reduced to metallic Ni with oxidization of carbon to $CO_x$ in carbothermal reduction process.[29, 30] It is noteworthy that there is a common phenomenon that CO was discovered in the reduction process, but the function of CO was rarely researched. As well, this process has not been tracked in situ, and the participated or the dominant reducing species with its specific function remain unclear.

In the present study, carbothermal reduction was employed to prepare stable ruthenium based catalysts for hydrogenation of itaconic acid. The catalytic performance and acid-resistance of carbothermal reduced Ru-based catalysts were tested compared with hydrogen reduced ones. The intermediate carbon contained species – CO released in situ were detected in the carbothermal reduction process. And the function of this efficient reducing agent was verified as well. Stability and resistance to acid of carbothermal reduced Ru-based catalysts was discussed with the possible postulation associated with the function of CO generated in situ.

## Experimental

### Catalysts preparation

5 wt% Ru based catalysts were prepared by the incipient wetness impregnation method. $RuCl_3$ (Shenyang Nonferrous Metal Research Institute) was dissolved in deionised water, and then activated carbon (AC, coconut shell, 80–100 mesh, Aladdin Industrial Inc. ) was added into the above solution under stirring. The above sample was treated by ultrasound for 3 minutes before impregnating for 24 h, after then the slurry was dried in oven at 110 °C overnight in air atmosphere. This sample was named as Ru(Cl)/AC. And then the sample was treated at a desired temperature of 250 °C, 350 °C and 450 °C in inert atmosphere such as $N_2$, He, or Ar, and then kept for 3 h, that is carbothermal reduction process. Such samples were named as Ru/AC-C-250, Ru/AC-C-350, Ru/AC-C-450 for example. In general, Ru(Cl)/AC carbothermal reduced at 450 °C in $N_2$ was marked shortly as Ru/AC-C, and that reduced in $H_2$ via the same temperature program was marked as Ru/AC-H. AC calcined at 900 °C in $N_2$ for 3 h was marked as AC900. AC physically mixed with fumed $SiO_2$ (Aladdin Industrial Inc.) by the molar ratio of 1:9 was marked as AC+$SiO_2$. Ru(Cl)/AC900, Ru(Cl)/$SiO_2$ and Ru(Cl)/(AC+$SiO_2$) were prepared as same as Ru(Cl)/AC.

### Catalysts characterization

Texture properties achieved from Nitrogen adsorption-desorption experiments conducted at -196 °C on Quantachrome Autosorb-1. The samples were outgassed at 300 °C for over 6 h before measurement. The surface area was obtained using the Brunauer-Emmett-Teller (BET) model for adsorption data in relative pressure range of 0.05 to 0.30. And the total pore volume was obtained at P/Po = 0.99 while the micropore volume and mesopore volume were calculated by HK and BJH method respectively. X-ray diffraction (XRD) patterns were investigated on a Rigaku D/Max 2500PC diffractometer with Cu-Kα radiation (λ= 1.5418Å) at a scan rate of $5^{o}$ $min^{-1}$ from $10^{o}$ to $85^{o}$ (2θ) at 40 kV/200 mA. Surface morphology of catalysts was determined by transmission electron microscopy (TEM) with a JEM-2000EX microscope operated at 120 kV. The surface chemical analysis was performed with X-ray photoelectron spectroscopy (XPS) on a Thermo ESCALAB 250Xi spectrometer by using AlKα radiation ($E_{hv}$= 1486.6 eV) operated at 15 kV and 10.8 mA as the excitation source. Content of Ru were measured on PerkinElmer ICP-OES 7300DV and calculated by average of two parallel samples.

The reduction process and property profiles of the catalysts were measured by temperature-programmed reduction (TPR) with hydrogen, carbon monoxide and inert gas performed on a Micromeritics Auto Chem II 2920 Chemisorption Analyzer with both thermal conductivity detector (TCD) and mass spectrometry detector (MS). The catalyst samples were first pretreated at 200 °C in argon flow to drive away the moisture and impurities. Afterwards, $H_2$/Ar or CO/He or He gas stream (25 $cm^3$/min) was switched on and the temperature was raised from 50 to 800 °C. In situ chemical absorbing and analyzing of the gas released in the reduction process was designed using chemical absorption reagent and titration methods (shown in Scheme S1).

### Catalytic hydrogenation of itaconic acid

Catalytic reaction was performed in a 50 mL autoclave (T316 Stainless Steel, Parr Instrument) equipped with an electronic temperature controller and a magnetic stirrer. In a typical reaction, 6 wt% itaconic acid aqueous solution and reduced catalyst with a desired molar ratio were introduced into the reactor, which then was purged several times with high pure $H_2$ and subsequentlypressurized up to 10-30 bar $H_2$ after sealing. It was heated to 50-100 °C and kept for 0.5-1 h with a vigorous stirring. As soon as the reaction stopped, the autoclave was cooled to room temperature in cold water bath.

The products were collected and analyzed by HPLC (Waters e2695) equipped with an UV/visible detector (Waters 2489) and a refractive index detector (Waters 2414). Itaconic acid and methylsuccinic acid were analysed using Waters Atlantis T3 column at 35 °C, and 0.013 mol/L $H_3PO_4$ aqueous solution mixed with 15% methanol was used as the mobile phase with a flow rate of 0.5 mL/min. The RID temperature was 30 °C and the UV wavelength was 210 nm. The itaconic acid conversion and the selectivity of methylsuccinic acid were calculated by the formulas through the internal standard calibration curves (Shown in S4).

## Results and discussion

## Characteristics and properties of prepared catalysts

Textural characteristics of supports and catalysts were evaluated from nitrogen adsorption-desorption measurements and the results listed in Table 1. A high BET surface area about 1130 $m^2$/gaccompanied with the total volume of 0.60 $cm^3$/g were obtained for AC sample. While the sample Ru(Cl)/AC had a much lower BET surface area and a smaller total pore volume, due to the blockage of some pores by the metal precursor ruthenium trichloride hydrate solution impregnated on AC. However, Ru/AC-C and Ru/AC-H samples had similar high BET surface area around 1080 $m^2$/g, which were a little less than that of supports but much better than Ru(Cl)/AC as a consequence of the metal precursor reduced and the blockage removed. In addition, it was notable that Ru/AC-C had a total pore volume of 0.70 $cm^3$/g, which was larger than others. That could be proposed as a result of reduction of metal species in or on the pores combined with loss of carbon species during the carbothermal reduction process. As a consequence, numbers of micropores were changed to large pores which made the total pore volume higher than that of AC and Ru/AC-H (shown in Table S1).

Carbothermal reduced and hydrogen reduced Samples were also investigated by TEM shown in Fig. 1. A phenomenon was obviously noted that particles were homogeneously distributed and average size was around 1.0 nm in both samples. The much small average particle size in the samples was probably due to the large surface area and abundant micropores of the supports conformed to the results in Table 1. Therefore it was supposed that carbothermal reduction has a little influence on the particle distribution and the average size at this temperature compared to the hydrogen reduced ones with the same supports.

The XRD patterns of catalysts reduced by different methods were shown in Fig. 2. The wide peak around 2θ of 25° was associated with the amorphous structure of activated carbon. The diffraction peaks at 2θ of 38.4°, 44.0° were attributed to Ru(100) and Ru(101) crystal planes (ICDD-JCPDS card No. 06-0663), while no peaks characteristic of ruthenium oxide appeared in the curves. Both Ru/AC-C and Ru/AC-H profiles showed the emergence of broad and poor diffraction peaks around 44° suggesting that Ru species supported on AC were reduced into metallic Ru in inert non-reducible atmosphere such as $N_2$ or He as well as reducible atmosphere $H_2$ at 450°C. This fact was consistent with the result of MS spectrum of $H_2$-TPR tests (Fig. S2). Besides, the broad diffraction peak of Ru (101) was perhaps due to uniformly distributed small Ruparticles associating with TEM images (Fig. 1).

**Table 1** Comparison of Physical property for different samples

| Sample | $S_{BET}$ ($m^2$/g) | Total Pore Volume ($cm^3$/g) |
|---|---|---|
| AC | 1130 | 0.60 |
| Ru(Cl)/AC | 842 | 0.54 |
| Ru/AC-C | 1080 | 0.70 |
| Ru/AC-H | 1090 | 0.62 |

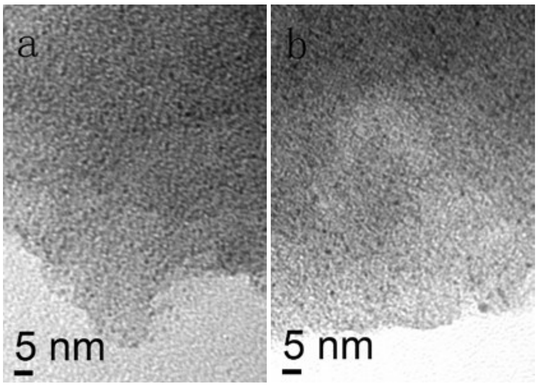


**Fig. 1** TEM images of (a) Ru/AC-C and (b) Ru/AC-H.

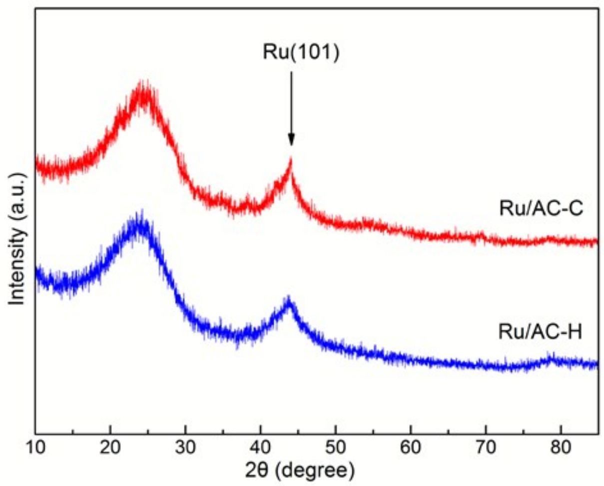


**Fig. 2** Powder XRD patterns of Ru/AC-H and Ru/AC-C.

## In situ generation and function of CO in carbothermal reduction process

The carbothermal reduction of Ru/AC at different temperatures was studied by $H_2$-TPR with both TCD and MS as detectors, and the profiles were shown in Fig. 3. There were two peaks around 180 °C and 230 °C in the TPR curves for Ru(Cl)/AC sample, which were attributed to reduction peaks of Ru species.[31-33] For Ru/AC-C-250 sample, the reduction peaks still appeared in the TPR curves, which meant that Ru species have not reduced to metallic Ru at that treating temperature. While for Ru/AC-C-350 and Ru/AC-C-450 samples, there were no apparent peaks appeared, indicating that Ru species had been carbothermal reduced completely. All the curves began to increase slowly at high temperature, which was related to gasification of carbon in $H_2$ catalysed by Ru species.[34] Thus, it was reasonable to conclude that the carbothermal reduction process could not occurred entirely below 250 °C, and Ru species were completely reduced into $Ru^0$ when carbothermal reduction temperature was above 350 °C.

It was known that carbon species played a vital role in the reduction of metal species at high temperature,[26] however, the major reducing agent and its specific function were not confirmed yet. Hence, to better understand the carbothermal reduction, experiments of in situ monitoring and analyzing

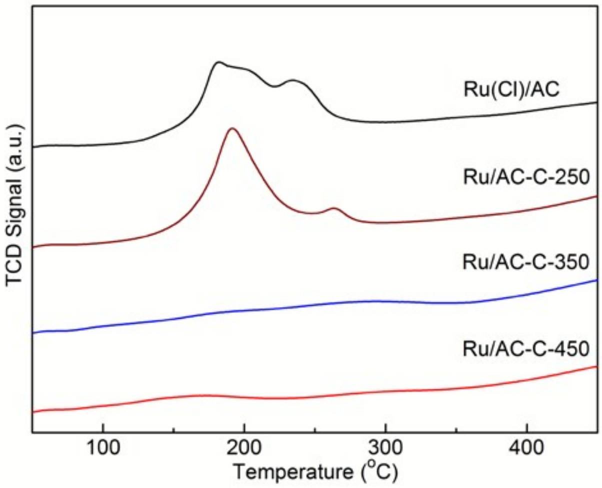


**Fig. 3** $H_2$-TPR profiles of Ru(Cl)/AC sample and Ru/AC-C samples which were carbothermal reduced at 250, 350, 450 °C respectively.

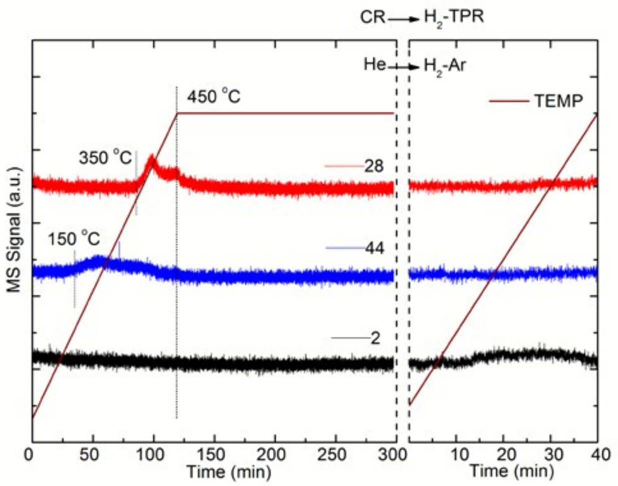


**Fig. 4** MS spectra of carbothermal reduction process of Ru(Cl)/AC in He, with subsequent $H_2$-TPR conducted on the chemical adsorption instrument with MS detector, and m/z of 28, 44 and 2 represent CO, $CO_2$, $H_2$ respectively.

were developed. 1) Carbothermal reduction of Ru/AC was carried out in inert atmosphere He on the chemical adsorption instrument with MS detector; after then $H_2$-TPR was subsequently conducted to investigate the degree of reduction, and the results were shown in Fig. 4. 2) In situ chemical absorbing and analyzing the gas released in the reduction process was designed using chemical absorption reagent and titration methods (shown in Scheme S1 and Table S2), and the results of produced $CO_2$ were presented in Table 2.

In experiment 1 of carbothermal reduction process, MS detector monitored two kinds of gases, whose m/z were 28, 44 attributed to CO and $CO_2$ respectively (as shown in Fig. 4). In the subsequent $H_2$-TPR test，no apparent peak appeared in each signal curve, including m/z of 28, 44 and 2 (which represent $H_2$). This result indicated that Ru species were totally reduced into metallic Ru in the former carbothermal reduction process. Released $CO_2$ and CO were probably produced from the oxided Ru precursors and surface oxygen-containing groups of activated carbon via REDOX reaction. $RuCl_3$ could be oxidized and decomposed easily, and transformed into ruthenium oxides and ruthenium oxychlorides or other Ru species when exposed or heated in air.[31-33] Ru(Cl)/AC and dried $RuCl_3$ were performed with XPS to investigate chemical states of Ru species. The spectra in the vicinity of the Ru3d and Ru3p peaks of these samples confirmed that there were $RuCl_3 \cdot xH_2O$ and $RuO_x$ formed in Ru(Cl)/AC (Details in S2.4, XPS spectra was shown in Fig. S3). Besides, it has been reported that surface oxygen-containing groups existed on activated carbon, and amounts of CO and $CO_2$ could be released in high temperature treatments.[35-37]. In conclusion, it can be inferred that the oxided Ru precursors and the surface oxygen-containing group of activated carbon, both were kinds of oxygen resource in the formation of CO for reduction of Ru species.

It could be learned from the profiles that $CO_2$ were detected from 150 °C with a gradually trend of first increasing and then decreasing, while CO appeared after 350 °C. Combined with the $H_2$-TPR profiles (Fig. 3), Ru species couldn't be carbothermal reduced completely below 350 °C. That means only when the extra released CO start to be detected (around 350 °C), the reduction reactions appeared to be completed. According to the previous literature, CO is an efficient reducing agent for metal.[38, 39] Moreover, the amount of released CO was much more than $CO_2$ during the temperature programmed desorption of activated carbon and carbon supported catalysts.[37, 40] It could be speculated that CO released below 350 °C participated in the reduction of Ru species, which helped to the produce of $CO_2$ at low temperature. As the reduction process progressed, the extra released CO was detected while the amount of $CO_2$ decreased.

Results of experiment 2 also showed that there were amounts of $CO_2$ released from both supports and catalysts displayed in Table 2. When calculated from the reduction reaction equations of Ru(Ⅲ) to $Ru^0$, double $CO_2$ were produced when CO was the reducing species compared to carbon reducing Ru(Ⅲ) (see the theoretical value of $CO_2$ in Table 2). The amounts of $CO_2$ calculated from the absorbing

**Table 2** Amounts of $CO_2$ produced in carbothermal reduction

| Sample | Theoretical value of $CO_2$[a] (mmol/g) | | Measured value of $CO_2$[b] (mmol/g) |
|---|---|---|---|
| | C as reductant | CO as reductant | |
| Ru(Cl)/AC | 0.32 | 0.63 | 0.56 |
| Ru(Cl)/AC900 | 0.32 | 0.64 | 0.54 |

a: Amounts of $CO_2$ calculated from the reduction reaction equations of Ru(III) to metallic Ru with C or CO as reducing species respectively.

b: Amounts of $CO_2$ produced in reduction calculated from the chemical absorption experiments in the carbothermal reduction process. (Details in S2)

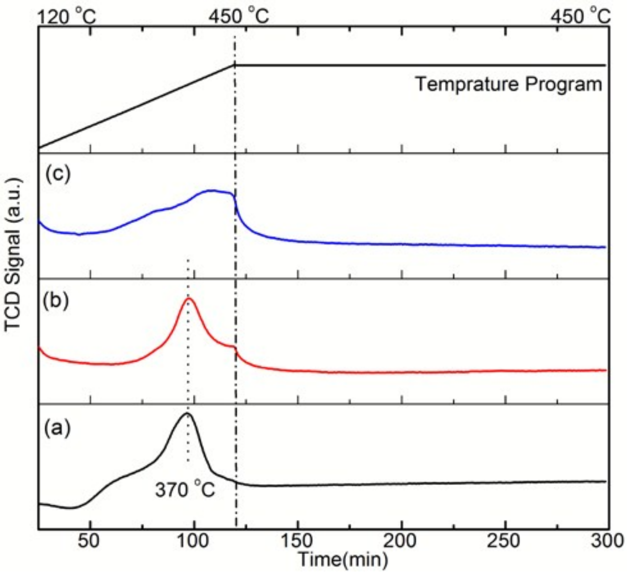


**Fig. 5** In-situ TPR profiles of the reduction process: (a) Ru(Cl)/$SiO_2$ reduced in 10% CO-He gas mixture; (b) Ru(Cl)/AC carbothermal reduced in He; (c) Ru(Cl)/(AC+$SiO_2$) reduced in He.

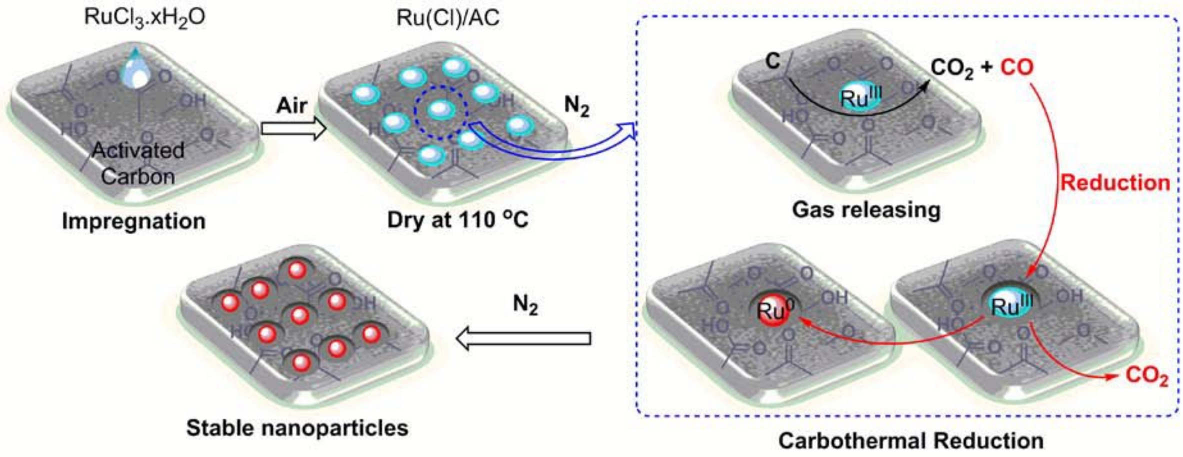
experiments were much more than that from supports (shown in Table S2), indicating that extra amounts of $CO_2$ were produced by the carbothermal reduction reaction. Apart from the amounts of $CO_2$ from supports, the extra parts of $CO_2$(that is the measured value of $CO_2$), were close to $CO_2$ produced by CO reducing trivalent ruthenium. From the above experiments results, we proposed that CO released in situ functioned as a reducing agent in the carbothermal reduction reaction of Ru species to metallic Ru. And extra CO may act as ligands adsorbed on the supports with the left unsaturated carbon atoms contacted with metallic Ru, which probably help to form stable particles.

To further understand the function of CO participated in the reduction reaction, another experiment was designed. Non-carbon catalysts Ru(Cl)/$SiO_2$ reduced by CO and carbon mixed catalysts Ru(Cl)/(AC+$SiO_2$) thermal reduced in inert atmosphere were explored and tested in the TPR experiment. The profiles were shown in Fig. 5. For Ru(Cl)/$SiO_2$, there was an obvious peak around 370 °C (Fig. 5a), which could be attributed to the CO reduction peak. For Ru(Cl)/(AC+$SiO_2$), a same reduction peak emerged as well below 450 °C (Fig. 5c). The results were similar to caborthermal reduction process of Ru(Cl)/AC (Fig. 5b). This phenomenon can infer that new CO produced in situ reduced Ru species into metallic Ru.

According to the above results, a possible mechanism for carbothermal reduction of Ru(Cl)/AC was proposed in Scheme 1. Ru precursor was first impregnated on AC support, and after dried in air at 110 °C, the precursor changed into Ru species including ruthenium oxides and chloride oxides.[31-33] Then in the inert atmosphere, the carbothermal reduction of the samples took place as temperature increased. At the beginning of the reduction, amounts of $CO_2$ and CO were produced from Ru precursor and surface oxygen-containing groups of activated carbon. Meanwhile the Ru species were reduced in situ by released CO gradually resulting in formation of flat and uniform particles. Afterwards more CO were released which completely reduced Ru species to fresh metallic Ru. During the carbothemal reduction, Ru atoms may be contacted with adsorbed CO and the unsaturated carbon atoms, and then rearranged into a novel tight stable configuration maintained uniform morphology of homogeneously dispersion.

### Catalytic performance in hydrogenation of itaconic acid

Hydrogenation of itaconic acid with carbothermal reduced Ru based catalysts was carried out in stainless autoclave at 50 °C for 0.5 h with 10 bar initial pressure of $H_2$, and recycled nine times. As a contrast, their analogues reduced by hydrogen were also tested. Both catalysts were reduced at 450 °C. The results were presented in Fig. 6. Ru/AC-H showed higher catalytic activity as the conversion reached 75.4% at the first time. However, the conversion had dramatically dropped down to 64.5% in the fourth time and then decreased to 53.0% at the ninth time. The selectivity of methylsuccinic acid was maintained above 95.0%. Comparatively, fresh Ru/AC-C samples got 51.2% of conversion in the first reaction, and showed a little fluctuation around an average percent of 51% during the nine recycling times, and then reached to 47.8% at the last time respectively. It also had an excellent selectivity of



**Scheme 1** The proposed schematic diagram for the carbothermal reduction process of Ru(Cl)/AC catalysts.

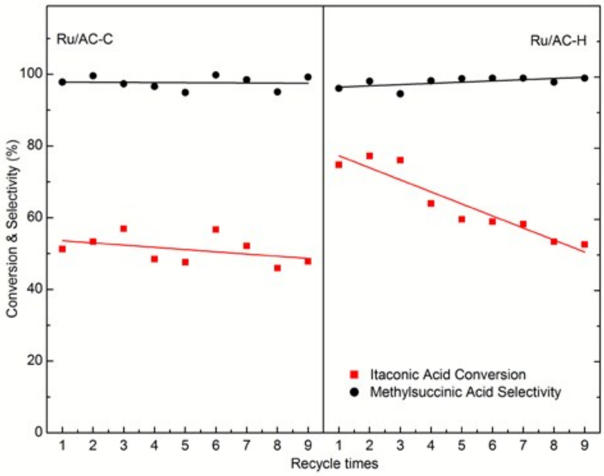


**Fig. 6** Comparison of catalyst resistance to acid for Ru/AC-C and Ru/AC-H in hydrogenation of itaconic acid.
Reaction conditions: 20 g 6 wt% itaconic acid aqueous solution, 0.1 g 5 wt% Ru catalysts, 10 bar initial pressure of $H_2$, 50 $^{o}$C, 0.5 h.

methylsuccinic acid with an average percent of 97.6%. Obviously, for the selectivity of methylsuccinic acid, there was no apparent difference in both samples. Ru/AC-C showed much little change on itaconic acid conversion with a difference of 3.4% while Ru/AC-H turned out to be a precipitous decline with a loss of 22.4% in nine times. It could be concluded that carbothermal reduced catalysts exhibited much better stability than hydrogen reduced ones.

It was known that catalytic activity generally was associated with the particle size related to the available amounts of active metal atoms. Ru/AC-H showed a little higher catalytic activity perhaps was because of smaller particle size.[26] The result of catalysts recyclability tests declared that Ru/AC-C was much stable. In addition, Ru contents in Ru/AC-C and Ru/AC-H after nine cycle tests were measured by ICP-OES, which were 3.8 wt% and 2.8 wt% respectively. That means carbothermal reduced sample had less leaching compared to hydrogen reduced samples, which had much lower Ru content after nine cycle tests. It was in accordance with activity change. It inferred that carbothermal reduction could be efficiently resistant to acid, and probably prevent the leaching of active sites during the catalytic process. The reason may be that CO in situ reduced Ru species during the carbothermal reduction process, leaving unsaturated carbon atoms coordinated with the new fresh Ru atoms forming the more stable Ru particles embedded on the support.[26] Therefore, such a process could influence in both stability and activity.

Though Ru/AC-C had a little lower catalytic activity under above conditions, it showed much better resistance to acid. Hence, to get higher conversion of itaconic acid and to further investigate its stability, we carried out the hydrogenation reaction under another condition (100 $^{o}$C for 1 h with 30 bar initial pressure of $H_2$). The results of six recycle reactions were shown in Fig. 7 and the HPLC profiles of products analyzing were presented in Fig. S5. It was apparently that the catalytic activities increased rapidly to 99% conversion of itaconic acid with 99% selectivity of methylsuccinic acid as shown in Fig. 7. More strikingly, there was no apparent difference in conversion and selectivity with no trend to decrease in the recycle tests of six times. In conclusion, the catalytic activity of Ru/AC-C in hydrogenation of itaconic acid can be increased to 100% by modulating the reaction conditions. Moreover, the resistance to acid of carbothermal reduced Ru/AC maintained well in higher temperature and longer reaction time. Above all, it could be issued that carbothermal reduced catalysts has good stability.

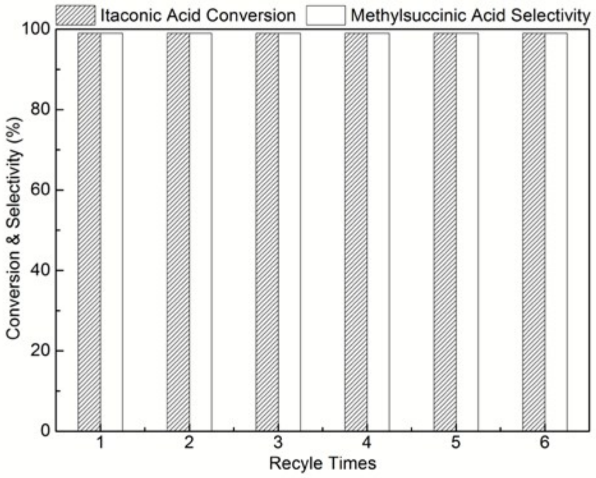


**Fig. 7** Catalysts performance and stability of Ru/AC-C in hydrogenation of itaconic acid at high reaction temperature with long reaction time.
Reaction conditions: 20 g 5 wt% itaconic acid aqueous solution, 0.2 g 5 wt% Ru catalysts, 30 bar initial pressure of $H_2$, 100 $^{o}$C, 1 h.

## Conclusions

Stable ruthenium based catalyst was prepared via carbothermal reduction for hydrogenation of itaconic acid. It showed much better resistance to acid with no obvious loss of activity and less leaching in recycling tests than hydrogen-reduced sample, which exhibited apparent decrease of 22% in conversion of itaconic acid. Carbothermal reduced catalysts could remain 99% conversion and 99% selectivity of methylsuccinic acid, and maintained good stability and acid-resistance in higher temperature and longer reaction time. Results confirm that the CO generated in situ on the surface of supports functioned as an efficient reducing agent in the carbothermal reduction process. Thus reducing reaction results in forming uniformly dispersed stable Ru nanoparticles. The carbothermal reduction method provides an alternative method for preparing catalysts with good resistance to acid which would be applied in a variety of acid hydrogenation reactions.

## Acknowledgements

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## Notes and references

1. M. Besson, P. Gallezot and C. Pinel, *Chem. Rev*., 2014, **114**, 1827-1870.
2. T. Klement and J. Buchs, *Bioresour. Technol*., 2013, **135**, 422-431.
3. M. Okabe, D. Lies, S. Kanamasa and E. Y. Park, *Appl. Microbiol. Biotechnol*., 2009, **84**, 597-606.
4. T. Willke and K. D. Vorlop, *Appl. Microbiol. Biotechnol.*, 2001, **56**, 289-295.
5. J. J. Verendel, O. Pamies, M. Dieguez and P. G. Andersson, *Chem. Rev*., 2014, **114**, 2130-2169.
6. F. M. A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer and W. Leitner, *Angew. Chem., Int. Edit.*, 2010, **49**, 5510-5514.
7. A. Primo, P. Concepcion and A. Corma, *Chem. Commun.*, 2011, **47**, 3613-3615.
8. G. Szollosi, K. Balazsik and M. Bartok, *Appl. Catal.,A*, 2007, **319**, 193-201.
9. F. Gelman, D. Avnir, H. Schumann and J. Blum, *J. Mol. Catal.A: Chem.*, 1999, **146**, 123-128.
10. T. Schmidt, W. Baumann, H. J. Drexler and D. Heller, *J. Organomet. Chem.*, 2011, **696**, 1760-1767.
11. T. Schmidt, H.-J. Drexler, J. Sun, Z. Dai, W. Baumann, A. Preetz and D. Heller, *Adv. Synth. Catal.*, 2009, **351**, 750-754.
12. H. W. Liu, F. Xin, L. M. Wu, M. Y. Huang and Y. Y. Jiang, *Polym. Advan. Technol.*, 2002, **13**, 210-215.
13. J. Jamis, J. R. Anderson, R. S. Dickson, E. M. Campi and W. R. Jackson, *J. Organomet. Chem.*, 2000, **603**, 80-85.
14. J. Jamis, J. R. Anderson, R. S. Dickson, E. M. Campi and W. R. Jackson, *J. Organomet. Chem.,*2001, **627**, 37-43.
15. S. Li, X. Wang, X. Liu, G. Xu, S. Han and X. Mu, *Catal. Commun.*, 2015, **61**, 92-96.
16. I. Volovych, M. Schwarze, T. Hamerla, J. Blum and R. Schomaecker, *J. Mol. Catal.A: Chem.*, 2013, **366**, 359-367.
17. R. Luque and J. H. Clark, *Catal. Commun.*, 2010, **11**, 928-931.
18. R. J. White, V. Budarin, R. Luque, J. H. Clark and D. J. Macquarrie, *Chem. Soc.Rev.*, 2009, **38**, 3401-3418.
19. W. Q. Yu, J. Xu, H. Ma, C. Chen, J. Zhao, H. Miao and Q. Song, *Catal. Commun.*, 2010, **11**, 493-497.
20. W. Q. Yu, J. Zhao, H. Ma, H. Miao, Q. Song and J. Xu, *Appl. Catal., A*, 2010, **383**, 73-78.
21. H. C. Ma, K. Teng, Y. H. Fu, Y. Song, Y. W. Wang and X. L. Dong, *Energ. Environ. Sci.*, 2011, **4**, 3067-3074.
22. Y. Chi, L. Zhao, Q. Yuan, X. Yan, Y. Li, N. Li and X. Li, *J. Mol. Catal.*, 2012, **22**, 13571-13577.
23. J. Li, L. Liu, Y. Liu, M. Li, Y. Zhu, H. Liu, Y. Kou, J. Zhang, Y. Han and D. Ma, *Energy Environ. Sci.*, 2014, **7**, 393-398.
24. K. Xiong, Y. Zhang, J. Li and K. Liew, *J. Energ. Chem.*, 2013, **22**, 560-566.
25. F. Su, F. Y. Lee, L. Lv, J. Liu, X. N. Tian and X. S. Zhao, *Adv. Adv. Funct. Mater.*, 2007, **17**, 1926-1931.
26. F. Su, L. Lv, F. Y. Lee, T. Liu, A. I. Cooper and X. S. Zhao, *J. Am. Chem. Soc.*, 2007, **129**, 14213-14223.
27. Y. Yang, L. Jia, B. Hou, D. Li, J. Wang and Y. Sun, *ChemCatChem*, 2014, **6**, 319-327.
28. Y. Yang, L. Jia, B. Hou, D. Li, J. Wang and Y. Sun, *Catal. Sci. Technol.*, 2014, **4**, 717-728.
29. Q. Song, F. Wang, J. Y. Cai, Y. H. Wang, J. J. Zhang, W. Q. Yu and J. Xu, *Energ. Environ. Sci.*, 2013, **6**, 994-1007.
30. Q. Song, J. Y. Cai, J. J. Zhang, W. Q. Yu, F. Wang and J. Xu, *Chin. J. Catal.*, 2013, **34**, 651-658.
31. A. Bossi, F. Garbassi, A. Orlandi, G. Petrini, L. Zanderighi,*Stud. Surf. Sci. Catal.*, 1979,**3**, 405-416.
32. P.G.J. Koopman, A.P.G. Kieboom, H. van Bekkum, *J. Catal.*, 1981, **69**, 172-179.
33. V. Mazzieri, F. Coloma-Pascual, A. Arcoya, P. L'Argentiere and N. S. Figoli, *Appl. Surf. Sci.*, 2003, **210**, 222-230.
34. P. G. J. Koopman, A. P. G. Kieboom, H. Vanbekkum and J. W. E. Coenen, *Carbon*, 1979, **17**, 399-402.
35. P. R. Wentrcek, B. J. Wood and H. Wise, *J. Catal.*, 1976, **43**, 363-366.
36. E. Gallegos-Suarez, M. Pérez-Cadenas, A. Guerrero-Ruiz, I Rodriguez-Ramos and A. Arcoya, *Appl. Surf. Sci.*, 2013, **287**, 108-116.
37. Y. Guo, L. Chen, D. Ma, D. Ye and B. Huang, *J. Energ Chem.*, 2013, **22**, 591-598.
38. M. C. Bronson and H. Y. Sohn, *Metall. Mater. Trans. B*, 1983, **14**, 605-615.
39. L. D. Pachon and G. Rothenberg, *Appl. Organomet. Chem.*, 2008, **22**, 288-299.
40. J. M. Rosas, J. Rodríguez-Mirasol and T. S. Cordero, *Energ. Fue* 2010, **24**, 3321-3328.