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RSC Advances

ARTICLE

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

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SUPPLEMENTARY INFORMATION

S1 Characterization of catalyst

S1.1 N_2 Physical Adsorption

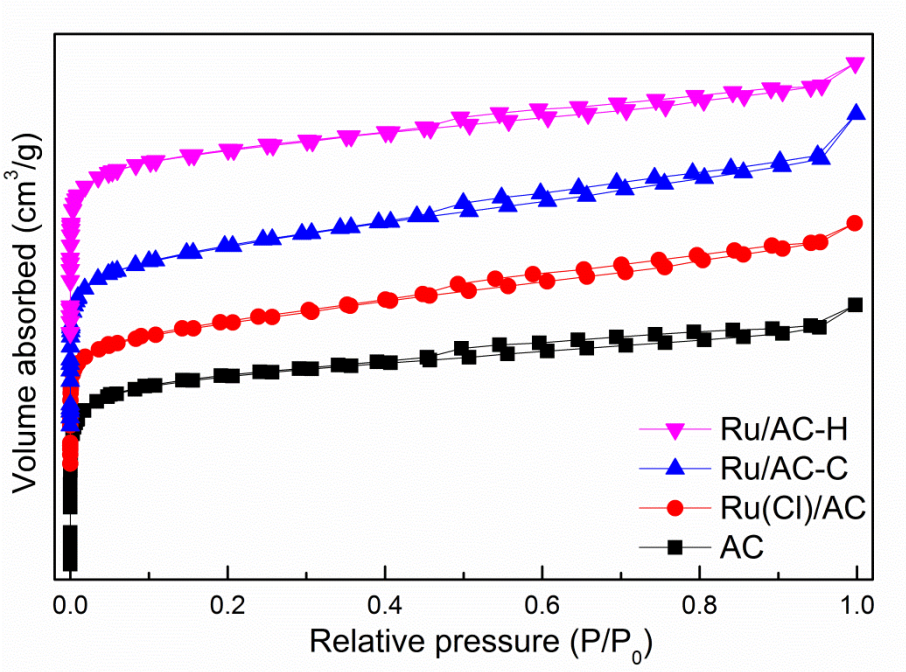


Fig. S1 N_2 physisorption of supports and catalysts

Table S1 Comparison of Physical property for different samples

Sample	S_{BET} (m^2/g)	Pore Volume(cm^3/g)		
		Total Pore Volume At P/Po = 0.99	Caculated by BJH method	Caculated by HK method
AC	1130	0.60	0.16	0.46
Ru/AC-C	1080	0.70	0.29	0.44
Ru/AC-H	1090	0.62	0.19	0.44

S2 Research of carbothermal reduction process

S2.1 MS spectrum of TPR tests

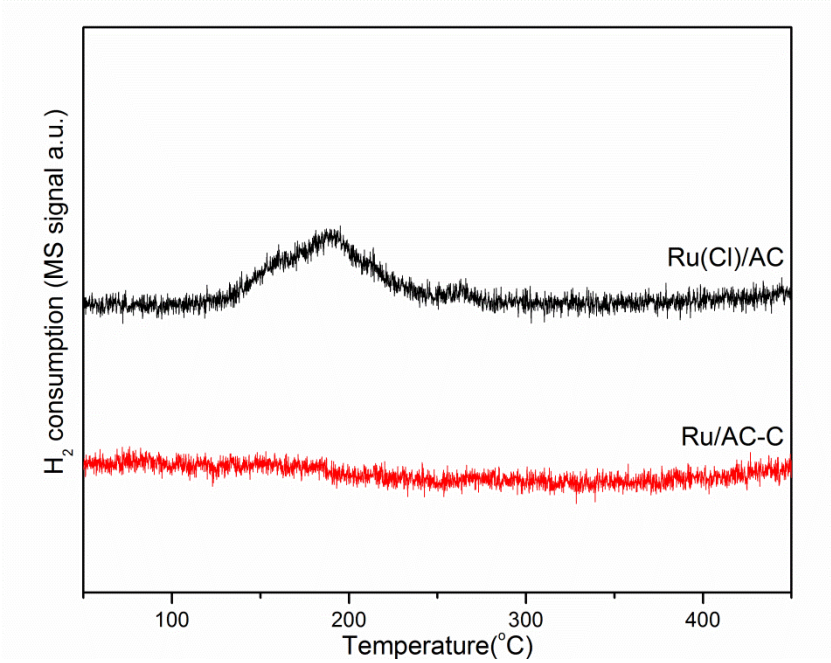


Fig. S2 MS profiles of H_2-TPR tests of Ru(Cl)/AC and Ru/AC-C in Fig.3

S2.2 Surface chemistry property of dried $RuCl_3$ and Ru(Cl)/AC

Surface chemistry property of as-synthesised samples was performed with XPS. The spectra in the vicinity of the Ru3d and Ru3p peaks of these samples were shown in the following Fig. S3. Due to the strong C1s peak from activated carbon around 284.6 eV overlap with characteristic peak of Ru3d transition, it was difficult to analysis the surface chemistry state of Ru species. The sample that $RuCl_3$ without carbon supports dried in air at 110 ^{o}C were prepared to research surface chemistry property of Ru precursors. As shown in Fig. S3, the middle peak at 284.6 eV was ascribed to C1s contamination peaks, which had lower intensity in dried $RuCl_3$. And there were two well-resolved peaks at 286.7 eV and 282.6 eV separated by approximately 4.1 eV corresponding to $Ru3d_{3/2}$ and $Ru3d_{5/2}$. It was found that there was a pair of two smaller peaks at 286.2 eV and 282.1 eV by peak-differentation-imitating analysis. That indicated there were at least two kinds of Ru chemical states. There were two pair peaks of $Ru3p_{1/2}$ and $Ru3p_{3/2}$ in Ru3p transition, which were in accordance with the above analysis. Such peaks were probably attributed to $RuCl_3 \bullet xH_2O$ and RuO_x as reported in literature.[1-4] Except the strong C1s transition, Ru(Cl)/AC had similar Ru3p and Ru3d peaks at the same binding energy with dried $RuCl_3$.

Reference:

1. A. Bossi, F. Garbassi, A. Orlandi, G. Petrini, L. Zanderighi,*Stud. Surf. Sci. Catal.*, **1979**,*3*, 405-416.
2. P.G.J. Koopman, A.P.G. Kieboom, H. van Bekkum, *J. Catal.*, **1981**, *69*, 172-179.
3. V. Mazzieri, F. Coloma-Pascual, A. Arcoya, P. L'Argentiere, N. S. Figoli, *Appl. Surf. Sci.*, **2003**, *210*, 222-230.
4. J. Y. Shen, A.Adnot, S. Kaliaguine. V., *Appl. Surf. Sci.*, **1991,** *51*, 47-60.

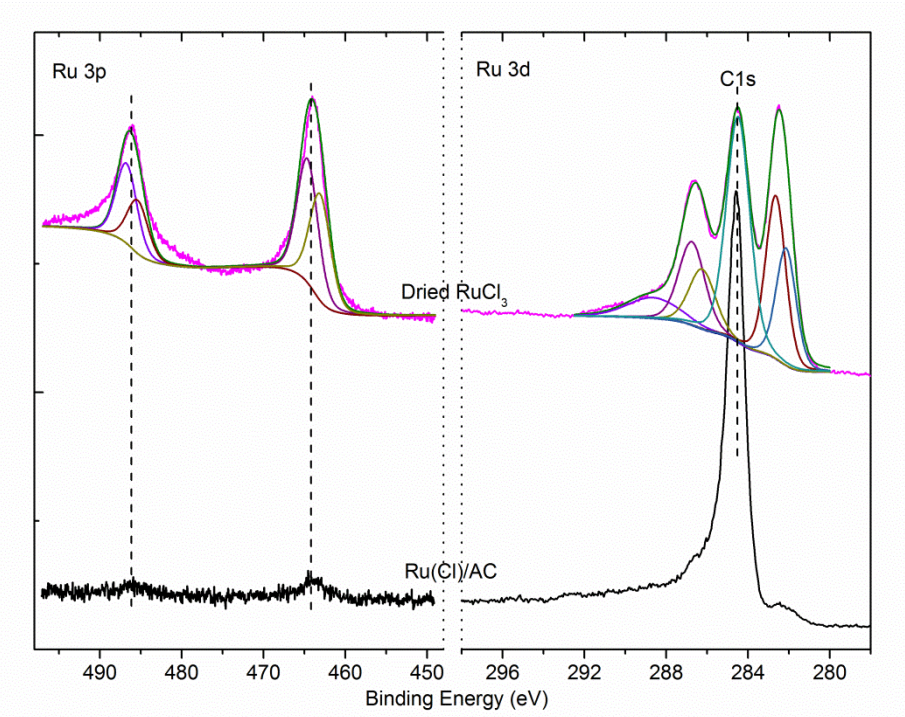
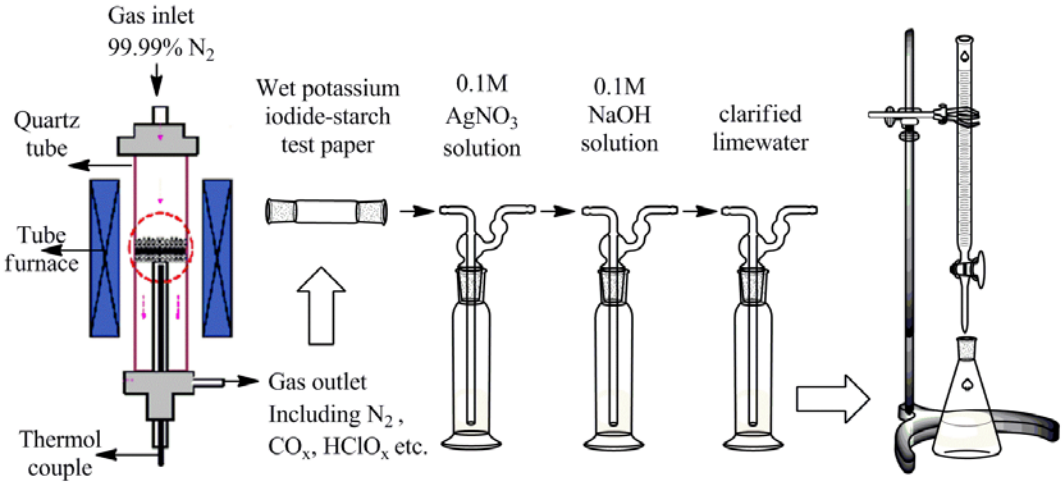


Fig. S3 XPS spectra of Ru3p and Ru3d transition in samples of dried $RuCl_3$, Ru(Cl)/AC

S3 In situ chemical absorbing and analyzing of the gas

S3.1 Scheme of in-situ chemical absorbing and analyzing instruments



Scheme S1 In situ chemical absorbing and analyzing of the gas released in the reduction process.

S3.2 Calculation of amounts of CO_2 via chemical methods

Table S2 Amounts of CO_2 calculated via chemical methods

Sample	Theoretical Ru content (mmol/g)	Theoretical value of CO_2[a] (mmol/g)		Total absorbed CO_2[b] (mmol/g)	CO_2 from support[c] (mmol/g)	Measured value of CO_2[d] (mmol/g)
		C as reductant	CO as reductant			
AC	--	--	--	1.23	--	--
Ru(Cl)/AC	0.42	0.32	0.63	1.61	1.05	0.56
Ru(Cl)/AC900	0.43	0.32	0.64	1.61	1.06	0.54

a: Amounts of CO_2 calculated from the reduction reaction of Ru(Ⅲ) to metallic Ru with C or CO as reducing species respectively. Ru^{III} + 3/4 C → Ru^0 + 3/4 CO_2; Ru^{III} + 3/2 CO → Ru^0 + 3/2 CO_2

b: Amounts of CO_2 absorbed using 0.1 M NaOH solution in the chemical absorption experiments and calculated from chemical titration of the absorption solution

c: Amounts of CO_2 released from the supports of catalysts using the results of AC in entry 1 for calculation.

d: Amounts of CO_2 produced in reduction calculated from the chemical absorption experiments, which equals the difference of total absorbed CO_2 minus CO_2 from support.

S4 Catalytic tests--hydrogenation of itaconic acid

S4.1 Standard curve of itaconic acid and methylsuccinic acid

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), using Waters Atlantis T3 column with aqueous H_3PO_4 solution mixed with methanol as the mobile phase. The itaconic acid conversion and the selectivity of methylsuccinic acid were calculated by the standard curves of internal standard method.

$$\text{Conversion of itaconic acid}(\%) = \left[1 - \frac{\text{Mole of unreacted itaconic acid}}{\text{Mole of initial itaconic acid}}\right] \times 100\ \%$$

$$\text{Selectivity of methylsuccinic acid}\ (\%) = \frac{\text{Mole of formedmethylsuccinic acid}}{\text{Mole of reacted itaconic acid}} \times 100\ \%$$

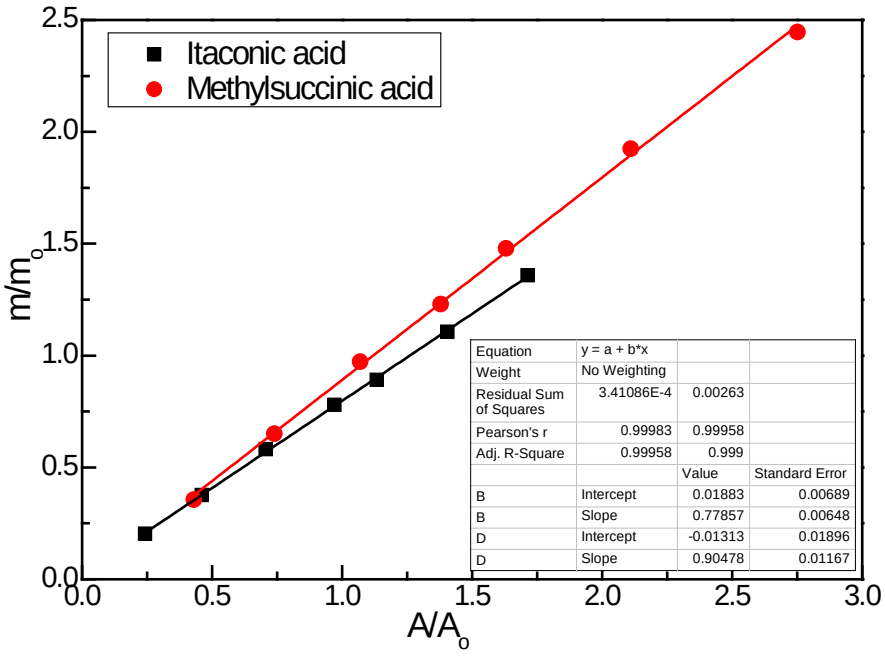


Fig. S4 Standard curve graphs of itaconic acid and methylsuccinic acid using RID detector

S4.2 HPLC profiles of itaconic acid and methylsuccinic acid

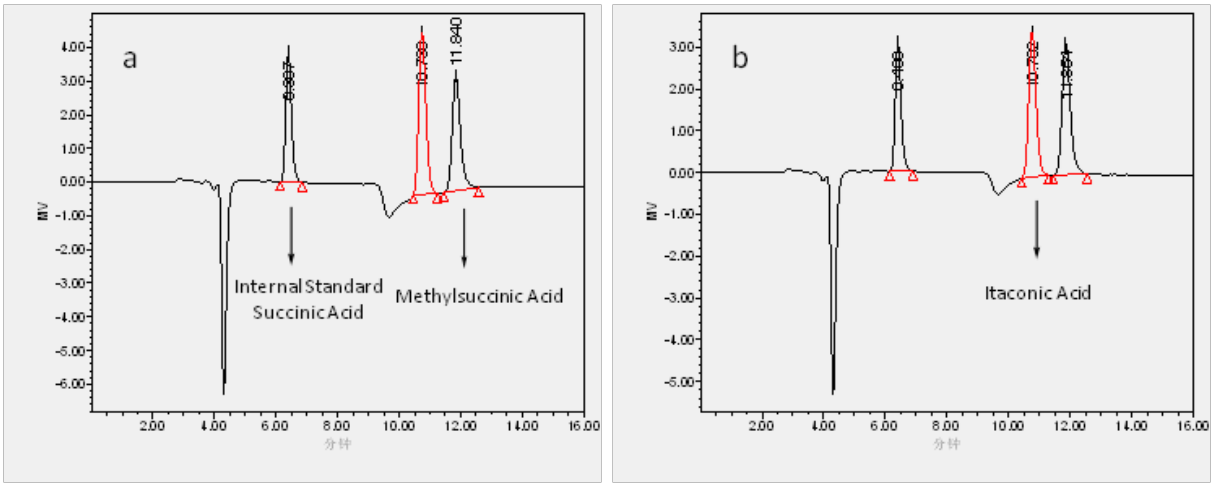


Fig. S5 HPLC profiles of products detection of the ninth recycling reactions with catalysts Ru/AC-C (a) and Ru/AC-H (b)

S4.3 HPLC profiles of products detection in six recycle tests

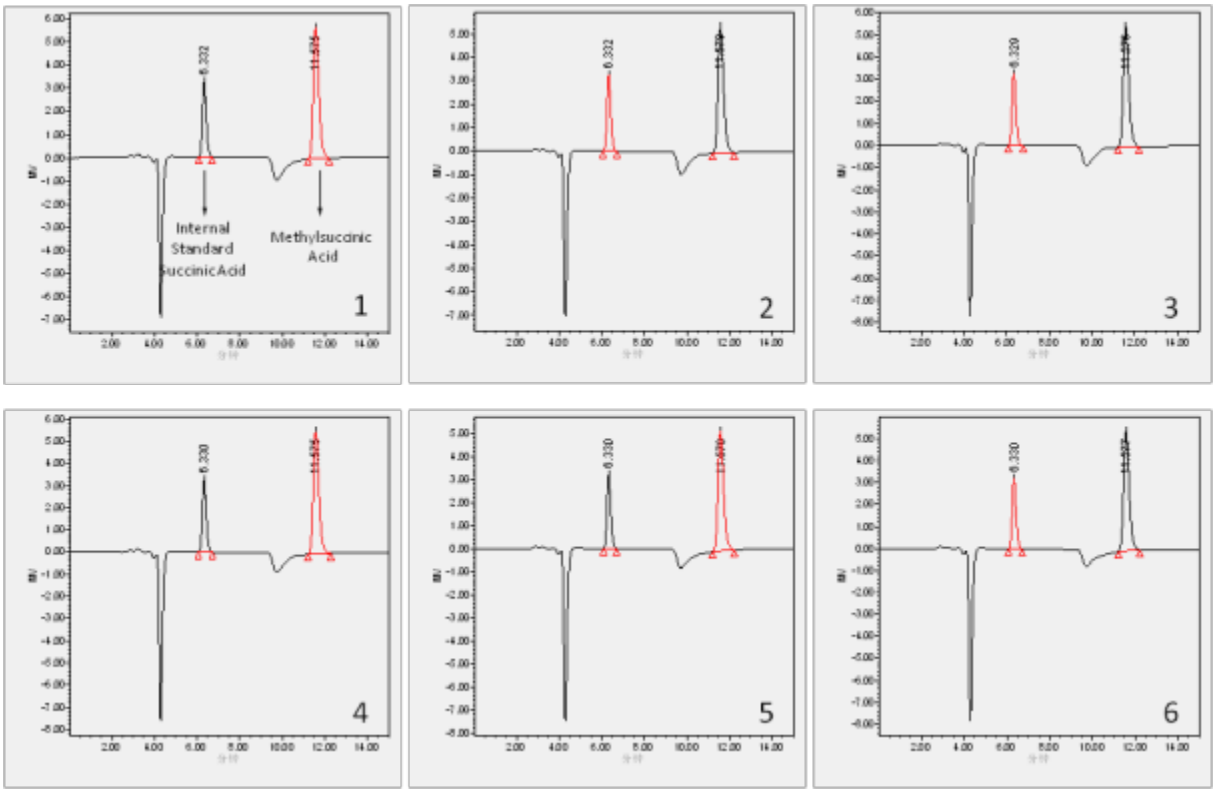


Fig. S6 HPLC profiles of products detection for Ru/AC-C in 6 recycle times