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Ru lonesome tonight? Immobilized ruthenium clusters (50 Ru atoms) in nanosized mesoporous zirconium silica were synthesized by using an impregnation method starting from an aqueous solution of RuCl₃. The Ru cluster catalysts were thermally stable at 500 °C and showed remarkable activity for the hydrogenation of furan derivatives in water at room temperature under 5 bar hydrogen pressure.



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Immobilized Ru Clusters in Nanosized Mesoporous Zirconium Silica for the Aqueous Hydrogenation of Furan Derivatives at Room Temperature

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Noble-metal clusters are important catalysts because of their unique structures and activities, which are associated with their metal—metal bonds.^[1] Numerous methods have been developed to encapsulate metal clusters within porous materials or polymers to protect the clusters against sintering.^[2] A common porous support is zeolite, owing to its intrinsic subnanometer pore diameters, which are similar to the size of the metal clusters and can confine and prevent the clusters from growing into big particles. This confinement allows metal clusters to activate reactants with small molecular sizes that are accessible to the pores.^[3]

Mesoporous silica provides an ideal support, owing to its large pore diameters, which are suitable for large-sized organic substrates and biomass derivatives.^[4] Ligand-stabilized metal precursors are usually used to anchor the clusters within the mesoporous channel with a low loading of the metal.^[5] Uniform mesoporous-silica-supported noble-metal clusters cannot be achieved by impregnation of the support in an aqueous solution of the metal salts because the pore diameter of mesoporous silica (>2 nm) is larger than the size of the metal clusters. The metal clusters are easily grown into big particles with a broad size distribution.^[6] The incorporation of heteroelements (Zr, Ti, Al, etc.) into mesoporous silica has been developed to disperse metal species.^[7] However, some metal particles still migrate towards the outside of the support during the reduction step with hydrogen, which causes their aggregation into big particles and, hence, the blocking of the entrance to the pore channels. Therefore, substantial challenges remain towards the goal of synthesizing uniform metal clusters that are immobilized within mesoporous silica from the corresponding metal salts.

Biomass becomes an increasingly important feedstock to produce fuels and chemicals for a sustainable future.^[8] Furan derivatives have been identified as the key building blocks to

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	Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201300316.

synthesize valuable chemicals.^[9] Besides its nontoxic and nonflammable properties, water is a desirable solvent because the furan derivatives are soluble under aqueous conditions.^[10] Several catalysts have been developed for the hydrogenation of furan derivatives in water, but high reaction temperatures or high hydrogen pressures are required to achieve high activities because of the low aqueous solubility of hydrogen.^[11]

Herein, immobilized ruthenium clusters (50 Ru atoms) in nanosized mesoporous zirconium silica (MSN-Zr) were synthesized by using an impregnation method, starting from an aqueous solution of $RuCI_3$. The Ru cluster catalyst showed remarkable activity for hydrogenation of furan derivatives in water at room temperature under 5 bar hydrogen pressure.

MSN-Zr-*x*, which has a uniform hexagonal pore structure, was synthesized by modification of our previously reported two-step procedure,^[12] in which *x* denotes the Si/Zr molar ratio (for the detailed preparation, see the Supporting Information). The morphology and pore structure are similar to those of nanosized mesoporous silica (MSN), as shown in the Supporting Information, Figures S1 and S2. IR, UV, and energy-dispersive X-ray spectroscopy (EDS) measurements confirmed the incorporation of Zr into the mesoporous silica (see the Supporting Information, Figures S3–S5).

Supported 5 wt.% Ru catalysts were synthesized by impregnating the supports with an aqueous solution of RuCl₃, followed by drying at 110° C in air and reducing in a flow of H₂ at 350 °C for 6 h. TEM images of Ru/MCM-41, Ru/MSN, Ru/MSN-Zr-20, and Ru/MSN-Zr-20-C (after calcination in air) and their corresponding particle-size distributions are shown in Figure 1. The Ru nanoparticles that were supported on commercial MCM-41 with long channels showed particle sizes that ranged from 2.0 to 8.0 nm (Figure 1 a), with an average size of 3.8 nm, which was similar to the XRD results (see the Supporting Information, Table S1). We found that smaller Ru nanoparticles were grown inside the pores of MCM-41, whereas some larger particles were attached onto the outer part of the support (Figure 1 a). Interestingly, if MSN with short channels was used, the average particle size decreased to 1.6 nm. Moreover, most of the Ru nanoparticles were highly dispersed (Figure 1b). However, some Ru nanoparticles escaped from the support, as shown in the dashed circles in Figure 1 b.

If MSN-Zr was used, the average particle size further decreased to 1.1 nm. Calculations^[13] revealed that approximately 50 Ru atoms were contained in a Ru cluster of size 1.1 nm. Moreover, the Ru clusters were stabilized inside the channels, that is, no escaped Ru clusters were found, as shown in Fig-

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Figure 1. TEM images and particle-size distributions of a) 5 wt.% Ru/MCM-41, b) 5 wt.% Ru/MSN, c) 5 wt.% Ru/MSN-Zr-20, and d) 5 wt.% Ru/MSN-Zr-20-C. Insets show HRTEM images of typical Ru clusters supported on MSN (b) and MSN-Zr (c).

ure 1 c and the Supporting Information, S6. In addition, there is no apparent loss of surface area compared to the original support (see the Supporting Information, Table S2), thus indicating that the support channels are fully open to the reactants. After calcination in air at 500 °C for 3 h, the average particle size of the Ru cluster was still 1.1 nm, thus confirming that the Ru cluster in MSN-Zr was thermally stable (Figure 1d). These results suggest that the Ru clusters that are supported on MSN-Zr are highly dispersed and stabilized inside the channel and are accessible to the reactants.

Figure 2a shows a HAADF image of the MSN-Zr-supported Ru catalysts. EDS element mapping of Si (Figure 2b), Zr (Figure 2 c), and Ru (Figure 2 d) was performed across interfaces (rectangle 1). Most of the Ru elemental map could be overlapped with that of Zr, thus indicating that most of the Ru clusters are attached around the enriched zirconium area.

To further study the chemical states of the Ru clusters and the zirconium-silica support, the 3d core-level spectra of both Ru and Zr were measured by in situ XPS. Figure 3 a shows a Ru $3d_{5/2}$ peak at 280.4 eV, which is assigned to metallic ruthenium once the Ru/MSN precursors are reduced at 350°C.^[14] The binding energy (BE) values of Ru 3d_{5/2} in the reduced Ru/ MSN-Zr-20 samples (280.9 eV) are slightly higher than that observed in Ru/MSN. These spectroscopic data indicate a positive charge on the ruthenium clusters, which results in the formation of $Ru^{\delta+}$ species.^[15] On comparing the BE (Zr 3d_{5/2}) value of MSN-Zr-20 to that after hydrogen reduction, the peak appears to be in the same state, as shown in Figure 3b. If ruthenium is located on the support, the Zr 3d_{5/2} peak of Ru/MSN-Zr-20 is shifted to higher binding energy by 0.9 eV. The variation in the BE values indicates that the Ru clusters that are anchored onto the MSN-Zr support are positively charged and induce the Zr in the supports to adopt a new chemical environment.^[16] The H₂-TPR profiles of RuCl₃ salt on different supports further con-



Figure 2. a) HAADF image of Ru/MSN-Zr nanospheres and EDS elemental maps of b) Si, c) Zr, and d) Ru.

firm that there is a strong interaction between the Ru cluster and the MSN-Zr support (see the Supporting Information, Figure S7).^[17] From these results, we concluded that $Ru^{\delta+}$ species and a new chemical environment around the Zr species were formed on the Ru/MSN-Zr-20 catalysts.

The difference between commercial MCM-41 and MSN is the channel length. We mimicked the impregnation process by using capillary sizes of 1 and 10 cm. This difference appeared after the drying process. There was a clear black deposition



Figure 3. In situ XPS studies of Ru/MSN, Ru/MSN-Zr-20, and MSN-Zr-20. a) Ru 3d spectra, which consist of Ru 3d_{5/2} and Ru 3d_{3/2} peaks. b) Zr 3d spectra, which consist of Zr 3d_{5/2} and Zr 3d_{3/2} peaks.

onto both ends of the long capillary, whereas the black deposition was more evenly distributed in the short capillary (see the Supporting Information, Figure S8). Based on these observations, we proposed a mechanism to explain the effect of the support on the size of the Ru clusters, as shown in Scheme 1.



Scheme 1. Proposed mechanism for the channel-length effect on the synthesis of the supported Ru catalysts.

We assumed that the surface concentration of the RuCl₃ solute was higher than that of the bulk solution, according to Gibbs' surface-excess theory.^[18] The Ru ions would be continuously deposited at the channel mouth during the drying process for the long-channel commercial MCM-41. The short-channel support MSN could increase the evaporation of water, based on thermogravimetric (TG) analysis, as shown in the Supporting Information, Figure S9. Therefore, most of the Ru ions stay

inside the channel, instead of undergoing deposition at the channel mouth. After Zr was added into the MSN, all of the Ru ions were immobilized inside the channel because of the strong interactions between Ru ions and the support. Thus, we conclude that both short channels and zirconium oxide improve the dispersion of Ru ions, thus leading to the anchoring of the ruthenium clusters inside the mesoporous channels with high dispersion and stability.

We performed the aqueous hydrogenation of 5-hydromethylfurfural (HMF) as a model reaction over various supported Ru and Ru-black catalysts with different particle sizes (see the

Supporting Information, Table S1). Conversions and product selectivities are listed in the Supporting Information, Table S3. The impact of Ru particle size on the overall catalytic hydrogenation of HMF is shown in Figure 4. The rate of hydrogenation of HMF increased slightly on decreasing the Ru particle size

> from 14 to 2 nm. If the particle size was smaller than 2 nm, the rate of HMF hydrogenation increased dramatically. The rate of HMF hydrogenation at a particle size of 1.1 nm was 21 h⁻¹, which was 34 times higher than that at a particle size of 14.4 nm. Fujitani et al.^[19] also reported that the hydrogen-dissociation activity of an Au/TiO₂ catalyst increased markedly if the Au particle size was below 2 nm.

> To understand the high activity of Ru clusters that are smaller than 2 nm, the specific rate is introduced to determine the number of moles of hydrogen molecules that react on each surface of the Ru cluster. Figure 4, inset, shows that the specific rate increased with decreasing size of Ru. This result indicates that the remarkable increase in the hydrogenation rate could not be exclusively attributed to a size effect. It has been reported that an electron-deficient metal cluster might form if the metal cluster is supported on acidic surface sites or oxide entities.^[21] Electron deficiency might only be the property of rather small metal particles, because the positive charge would be shared among hundreds of metal atoms with large particle sizes.^[15] Electron deficiency affects the

chemisorption and enhances the hydrogenation activity of the metal clusters.^[22] The NH₃-TPD of MSN-Zr indicates there are acidic sites on the support surface (see the Supporting Information, Figure S10) and the XPS analysis suggests that the Ru^{$\delta+$} species are formed on the Ru/MSN-Zr catalysts. Therefore, we presume that the supported Ru clusters on MSN-Zr become electron deficient if the particle size is smaller than 2 nm. The high hydrogenation activity of 1.1 nm Ru clusters is

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Figure 4. Plot of the turnover frequencies (TOFs), based on the H₂-consumption rate, of HMF hydrogenation as a function of the size of the Ru particles on various supports. The total TOFs were simply defined as the total moles of H₂ converted per mole of Ru per hour. Specific rate was defined as the number of moles of hydrogen molecules that reacted at each surface per hour; the total surface area of the Ru nanoparticles was determined by assuming a spherical shape.^[20]

not solely attributed to small size, but also to the electron-deficient effect.

Control of the selectivity of the products on the Ru cluster catalyst was also studied, as shown in the Supporting Information, Figure S13. 2,5-Dihydroxymethylfuran (DHMF) is the main product at a reaction temperature of 25 °C, whereas 1,2,5-hexanetriol (1,2,5-HT) becomes the main product on increasing the temperature to 100 °C. Conversely, Alamillo et al.^[10b] reported that 1,2,5-HT was detected as a by-product if the aqueous hydrogenation of HMF over Ru/SiO₂ was performed at 130 °C. In our catalytic system, the opening of the furan ring predominates, rather than the hydrogenation reactions of the aldehyde or the furan ring, during the aqueous conversion of HMF at high temperatures.

After the aqueous hydrogenation reaction ($25 \,^{\circ}$ C, 5 bar H₂, 4 h), the Ru/MSN-Zr catalyst was separated from the reaction mixture by centrifugation and this catalyst was reused in subsequent runs under identical reaction conditions; the results are shown in the Supporting Information, Figure S14. The catalytic conversion of HMF was still observed after five cycles. Importantly, TEM analysis of the Ru catalyst after the fifth run indicated that the mesoporous structure of the support and the particle size of the Ru cluster remained unchanged.

The use of the Ru cluster catalyst was further extended to the hydrogenation of a series of furan derivatives, including furfural, 5-ethoxymethyl-2-furfural (EMF), and 5-methyl-2-furfural (MFF, Table 1). These four furan derivatives were hydrogenated into furan alcohol and tetrahydrofuran alcohol at room temperature with high activities. These results show that Ru cluster catalyst has high activity for the hydrogenation of furan derivatives in water at room temperature.

In conclusion, we have immobilized uniform Ru clusters within nanosized mesoporous zirconium silica with 5 wt.% Ru loading by using an impregnation method starting from an aqueous solution of RuCl₃. These Ru clusters were highly dispersed and stabilized within the mesoporous channels and



[[]a] Reaction conditions: Substrate (0.1 g), Ru/MSN-Zr-10 (2.47×10^{-5} mol Ru), water (9.9 g), 25 °C, H₂ (5 bar), 4 h at 1000 rpm. [b] Conversions of the furan derivatives. [c] Selectivities for the corresponding hydrogenated products.

were accessible to substrates. The catalyst showed remarkably high activity for the hydrogenation of furan derivatives in aqueous solution at room temperature. The control of selectivity of the products on the Ru cluster catalyst could be achieved by simply adjusting the reaction temperature. We proposed that the small size and electron deficiency of the Ru clusters contributed to their high activity. The reusability experiments and calcination tests showed that this catalyst was very stable. Although the underlying mechanism of the high thermal stability of Ru cluster on Ru/MSN-Zr is not yet fully clear, it could lead to the development of a new group of highly stable, practically relevant metal cluster catalysts.

Experimental Section

Synthesis of the Ru-containing catalysts

The synthesis of nanosized mesoporous zirconium silica (MSN-Zr-*x*, in which *x* denotes the Si/Zr molar ratio) was performed by modification of our reported method.^[12] The detailed procedure is described in the Supporting Information, Section S1. A series of supported Ru catalysts were typically prepared by impregnating the supports with an aqueous solution of RuCl₃, followed by drying in air at 110°C and reduction in a flow of H₂ at 350°C for 6 h. Ru/MSN-Zr-20 was also calcined in air at 500°C for 3 h to estimate the thermal stability of the supported Ru clusters, denoted as Ru/MSN-Zr-20-C. Ru black (Strem Chemicals, 99.9%), which was used for the control reactions, was activated under different conditions, that is, it was reduced in a flow of H₂ at 200°C for 2 h (denoted as Ru black-200) or calcined at 500°C under a N₂ atmosphere for 3 h and subsequently reduced in a flow of H₂ at 350°C for 6 h (denoted as Ru black-500).

Characterization

The particle size and shape were analyzed by TEM on a JEM-2000EX microscope that was operated at 120 kV. The micromorphology and composition of Ru/MSN and Ru/MSN-Zr were determined on a FEI Tecnai G^2 F30 S-Twin microscope from HRTEM and HAADF images and elemental maps. In situ XPS spectra for the chemical states of ruthenium and zirconium were recorded on

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a VGESCALAB MK2 spectrometer by using AlK_{α} radiation (E_{hv} = 1486.6 eV) operated at 12.5 kV and 250 W as the excitation source. The temperature-programmed reduction of hydrogen (H₂-TPR) and the temperature-programmed desorption of ammonia (NH₃-TPD) were recorded on a Micromeritics Autochem II 2920 instrument that was equipped with a thermal conductivity detector (TCD) and an on-line mass detector. XRD patterns were performed on a Rigaku D/Max 2500PC diffractometer with CuK_{α} radiation (λ = 1.5418 Å) and used for calculating the Ru particle sizes based on the Scherrer equation. Nitrogen-physisorption experiments were performed on a Quantachrome Autosorb-1 apparatus at -196 °C. To identify the incorporation of zirconium ions into the MSN framework, the as-synthesized MSN and MSN-Zr materials were characterized by FTIR spectroscopy and diffuse-reflectance UV/Vis spectroscopy (UV/Vis DRS).

Hydrogenation of the furan derivatives

The catalytic activity of the Ru catalysts was studied by using the aqueous hydrogenation of 5-hydroxymethylfurfural (HMF) as a model reaction. The reactions were performed in a 50 mL autoclave (T316 Stainless Steel, ASME SA-479, Parr Instrument) under an initial H_2 pressure of 5 bar at 25 °C. After the reaction, the Ru/ MSN-Zr catalyst was centrifuged from the solution, washed with water, and reused four more times. The reaction temperature and other furan derivatives were also considered. The products were identified by GCMS and by ¹H NMR and ¹³C NMR spectroscopy. An Angilent 7890A gas chromatograph system that was equipped with an Angilent 19091j-323 capillary column (30 m \times 530 $\mu m \times$ 1.5 µm) was used for product quantification. The measured reaction rates, in units of hydrogen that was consumed, as derived from the products per mole of Ru per hour, are reported as the total TOFs. The surface-specific hydrogenation rate is estimated by assuming that the Ru nanoparticles have a spherical shape and the deduced equations are listed in the Supporting Information, Section S2.

Acknowledgements

We acknowledge financial support for the National Natural Science Foundation of China (21233008, 21103174, and 21203183), the Hundred Talents Program of the Dalian Institute of Chemical Physics (DICP), and the State Key Laboratory of the Catalysis Program of the DICP (R201110).

Keywords: biomass · cluster compounds · hydrogenation · mesoporous materials · ruthenium

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Received: April 26, 2013 Published online on ■■ ■, 0000