

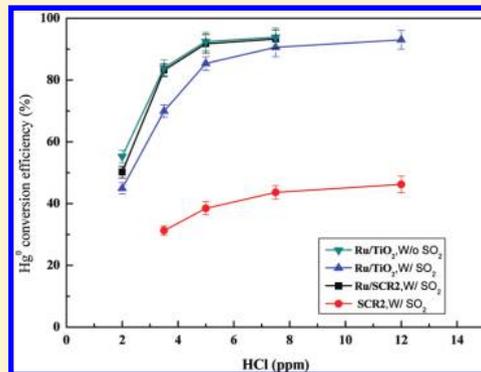
Significance of RuO₂ Modified SCR Catalyst for Elemental Mercury Oxidation in Coal-fired Flue Gas

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Supporting Information

ABSTRACT: Catalytic conversion of elemental mercury (Hg⁰) to its oxidized form has been considered as an effective way to enhance mercury removal from coal-fired power plants. In order to make good use of the existing selective catalytic reduction of NO_x (SCR) catalysts as a cobenefit of Hg⁰ conversion at lower level HCl in flue gas, various catalysts supported on titanium dioxide (TiO₂) and commercial SCR catalysts were investigated at various cases. Among the tested catalysts, ruthenium oxides (RuO₂) not only showed rather high catalytic activity on Hg⁰ oxidation by itself, but also appeared to be well cooperative with the commercial SCR catalyst for Hg⁰ conversion. In addition, the modified SCR catalyst with RuO₂ displayed an excellent tolerance to SO₂ and ammonia without any distinct negative effects on NO_x reduction and SO₂ conversion. The demanded HCl concentration for Hg⁰ oxidation can be reduced dramatically, and Hg⁰ oxidation efficiency over RuO₂ doped SCR catalyst was over 90% even at about 5 ppm HCl in the simulated gases. Ru modified SCR catalyst shows a promising prospect for the cobenefit of mercury emission control.



INTRODUCTION

Mercury has been listed as a hazardous and toxic pollutant under Title III of the 1990 Clean Air Act Amendments (CAAA) in the United States.¹ Based on the 25th Governing Council Session of United Nations Environment Programme (UNEP), the Negotiation to launch the UNEP Mercury Treaty has been initiated, and it is expected to be finalized in 2013.² Coal-fired power plants are the major anthropogenic mercury emission sources in China and The U.S. because of the huge coal consumption for power generation.^{1–3} Therefore, it is stringent to find any effective ways to reduce mercury emission from coal-fired utilities.

Mercury emission from coal-fired flue gas generally presents in three forms, elemental mercury (Hg⁰), gaseous oxidized mercury (Hg²⁺) and the particulate-bound mercury (Hg^p), mainly in oxidized form).^{4,5} The distributions of these forms are mainly dependent on the chlorine content in coal and the combustion conditions. With the existing air pollution control devices (APCD), most of the oxidized and particulate-bound mercury can be removed as the cobenefit, for instance, Hg^p will be effectively captured, along with fly ash particles, in electrostatic precipitators (ESPs) or baghouses; Hg²⁺ is soluble in water and therefore it can be removed efficiently by wet flue gas desulfurization equipments (WFGD). However, Hg⁰ is the most difficult to be removed because of its high volatility and low solubility in water. The conversion of Hg⁰ to its oxidized form can thus facilitate its capture from the flue gas by APCD.^{6–9}

Some transition metal catalysts, including those for the selective catalytic reduction of nitric oxides (SCR) have been observed to be helpful to the oxidation of Hg⁰ to Hg²⁺ when

there existed sufficient HCl in the flue gases.^{7,10–12} Mn/Al₂O₃ and Mo modified catalysts have been observed to display high Hg⁰ catalytic efficiency in the flue gas.^{10,11} Some noble metal catalysts, such as gold (Au) and palladium (Pd), have also been tentatively used as catalysts for elemental mercury conversion,¹² but they are too expensive for industrial applications. With the spread of SCR installation in coal-fired power plant for NO_x emission control, how to make good use of SCR catalyst for Hg⁰ conversion has been paid more attention.^{8,13–17} However, it has been observed that the conventional SCR catalysts were not effective enough for Hg⁰ conversion in the flue gas burnt the low chlorine coal. Moreover, most flue gas with high Hg⁰ distribution was just lacking in HCl and the design of the traditional SCR catalyst without the intention for Hg⁰ conversion. Also, SO₂ and ammonia have been observed to inhibit the oxidation of Hg⁰ over the conventional SCR catalysts.¹⁶ Therefore, how to enhance the catalytic activity for Hg⁰ oxidation at low level of HCl (e.g., <10 ppm) has become an important research scope to the cobenefit performance of SCR catalysts.

It has been recognized that the oxidation of Hg⁰ over catalysts in the presence of HCl might experience series reactions, such as Deacon reaction (through which HCl can be oxidized to Cl₂ or Cl atom by oxygen) or Mars-Maessen mechanisms.^{7,10,16} The latest research has indicated that RuO₂ over TiO₂ has been

Received: January 19, 2011

Revised: May 31, 2011

Accepted: May 31, 2011

Published: June 10, 2011

proved to be a very promising catalyst for Deacon reactions, through which HCl can be converted to Cl_2 effectively.^{18,19} So RuO_2 is expected to be a potential catalyst for Hg^0 conversion in the presence of HCl. Since the traditional SCR catalysts often employ TiO_2 as the carrier, it is possible to introduce RuO_2 to SCR catalyst for its multipurpose. In addition, the commercial price of Ru was just about 10–20% of that of Pt or Pd even though it is usually listed as noble metals, and the cost of the catalyst with low content of RuO_2 is acceptable in application. However, the roles of RuO_2 as a catalyst by itself or cooperated with other components for Hg^0 oxidation have never been involved in the previous research. Therefore, the performance of RuO_2 over TiO_2 as the catalyst of Hg^0 conversion was investigated, and it was tentatively used to modify SCR catalyst to improve the cobenefit of Hg^0 conversion from SCR catalysts at low HCl concentration. Meanwhile, the behaviors of the modified SCR catalyst in the reduction of NO_x , the oxidation of SO_2 , and the tolerance to SO_2 and NH_3 were also considered. The catalysts were characterized with different techniques, such as BET, XRD, ICP, XPS, etc.

EXPERIMENTAL SECTION

Materials. Commercially available TiO_2 powder was mainly used as the carrier of various catalysts, which is a standard material for all purposes (Degussa P25) and contains anatase and rutile phases in a ratio of about 3:1.²⁰ The original powder consisted of TiO_2 particles with 25–85 nm of the diameter. All chemicals used for the catalysts preparation were of analytical grades, and purchased from Sigma-Aldrich Co. and Sino-pharm Chemical Reagent Co. The Gases of SO_2 (100%), ammonia (20%) and HCl (5000 ppm) were produced by Dalian Date Gas Co. In order to evaluate the performance of the typical SCR catalyst for Hg^0 conversion, a commercial available SCR catalyst (V-W/ TiO_2 , denoted as SCR₂) was used as the reference, in which WO_3 (about 4.2%), V_2O_5 (about 0.52%) and TiO_2 (as the carrier). Meanwhile, a self-made SCR catalyst consisted of 1% of tungsten oxide and 1% of V_2O_5 (denoted as SCR₁) was used as the comparison.

Catalysts Preparation. Several TiO_2 -supported catalysts, which included Ru/ TiO_2 , Mn/ TiO_2 , Cu/ TiO_2 , V/ TiO_2 , W/ TiO_2 , and Cr/ TiO_2 were tested, and the weight percentage of the metallic oxides to TiO_2 was set at about 1% for the single metallic catalyst. Meanwhile, W-V/ TiO_2 , Ru-V/ TiO_2 , Ru-W-V/ TiO_2 , and Ru/SCR₂ were also tested as well, in which the weight percentage of RuO_2 , WO_3 and/or V_2O_5 was set at 1%, respectively, if it was not stated clearly. All TiO_2 supported or modified SCR catalysts were prepared by the multi-impregnation process to ensure all the components in the solutions to be impregnated on the carrier.^{12,13} The dried catalysts were calcined at 673 K for 2 h and at 773 K for 2 h in air.

Catalytic Activity Evaluation. The catalytic activity was evaluated in a fixed-bed reactor (a quartz tube, with the inner diameter of 5 mm), in which 30 mg of the catalyst (40–60 meshes particles, with the bulk volume of 0.051 mL) was filled. The simulated flue gases compositions were prepared in situ, and Hg^0 vapor was prepared from the Hg^0 permeation unit and was blended with the gases before they entered the reactor.¹⁰ The reactions were mainly performed under atmospheric pressure and at 423–623 K which was controlled by a tubular-furnace. The gas flow rate was 40 L/h corresponding to a space velocity (SV) of $7.9 \times 10^5 \text{ h}^{-1}$ for Hg^0 conversion tests, which was by far higher than that for the actual SCR operation (4000–10 000 h^{-1}).

Employing high SV was based on two considerations: first, the gas–solid contacting condition in a fixed bed was much better than that in honeycombs or plates catalyst configuration; second, only the tail section of SCR in low ammonia environment may be effective to the catalytic conversion of Hg^0 , which corresponded to a higher SV than that for SCR operation. The inlet Hg^0 concentration in the gas was controlled at about 50 ppbv, which was helpful to shorten the initial adsorption time and to minimize the relative error from the continuous data acquisition. The continuous monitor of Hg^0 concentration in the effluent stream and the balance tests of mercury before and after the conversion were also similar to our previous study,¹⁰ and the total mercury across the reactor appeared to be well balanced (see S1.1 and Figure S1 in the Supporting Information (SI)). The concentration of NO and SO_2 were measured with the flue gas analyzer (Testo 350-Pro). HCl, NH_3 and Cl_2 at low concentration were analyzed with specific detecting tubes (Gastec). SO_3 in the gas across the catalysts was trapped according to EPA method 8, in which 80% isopropyl alcohol (IPA) aqueous solution was as a trapping solution for gaseous SO_3 .²¹ Ionic chromatography (Metrohm-MIC) was used to quantitatively measure the concentration of sulfate in the solution.

Characterization of the Catalysts. To determine the crystals species distribution in the catalyst, X-ray diffraction (XRD) measurements were carried out with a diffractometer (D/max-2200/PC, Rigaku, Japan) using Cu–K α radiation. ICP analysis (Iris Advantage 1000, Thermo) was used to measure Ru contents in the prepared catalysts. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) measurements were used to determine the Ru3d5 binding energies with Al K α radiation ($h\nu = 1486.6 \text{ eV}$). Transmission electron microscopy (TEM) was used to investigate microstructures of the catalysts with an electron microscope (JEM-2010, JEOL, Japan). With the attachment of the energy dispersive X-ray Spectrometer (EDX), the precise elemental composition of materials can be obtained with high spatial resolution. The specific surface area of the catalysts was tested using Brunauer–Emmett–Teller (BET) method (ASAP 2010, Micromeritics Inc.). In order to investigate the redox performance of various catalyst, hydrogen temperature program reduction (H_2 -TPR) experiments were carried out on a TPR-5000 (Tianjin Xianquan) by increasing the temperature from 50 to 900 °C at a rate of 10 °C/min.

RESULTS AND DISCUSSION

Character of the Prepared Catalysts. The BET area were determined to be about 53.6 m^2/g , 46.1 m^2/g , 48.4 m^2/g and 59.9 m^2/g for TiO_2 , Ru/ TiO_2 , Mn(1%)/ TiO_2 and Ru(1%)/SCR₁, respectively. The content of Mn, Ru and other metals in the catalysts were verified with ICP analysis, and the actual Ru contents were consistent with the expected value in preparation (within 15% of the relative error, Table S1 in SI). The XRD patterns of TiO_2 (Figure S2 in SI) indicates that TiO_2 (Degussa P25) has two crystal types, anatase and rutile, respectively. In addition, TiO_2 in SCR₂ and Ru/SCR₂ is mainly in the form of anatase. The XRD pattern of Ru/ TiO_2 and Ru/SCR₂ shows a very weak peak of RuO_2 at the two theta degree of 35.1, while the other peak may be included in the strong peak at the two theta degree of 54. By comparing with the reference spectrum, Ru mainly presented in the form of RuO_2 . The weak peak of RuO_2 indicates that most RuO_2 on TiO_2 is well dispersed in noncrystalline form.

TEM image (Figure 1) confirms the crystalline TiO_2 and SCR_2 particles are between 20 and 100 nm. Also, the SAED patterns of Ru/TiO_2 (at the right down corner of TEM pictures) showed that Ru/TiO_2 appears to be the poly crystal diffraction rings within the same scanned surface area, which indicated the particles of RuO_2 are very small. Moreover, the energy dispersive X-ray Spectrometer (EDX) analysis (at the left up corner of TEM pictures) also indicated that the even dispersion of RuO_2 on the surfaces of TiO_2 or SCR_2 nanoparticles.

$\text{RuO}_2/\text{TiO}_2$ as the Monometallic Catalysts. The catalytic oxidation efficiencies of Hg^0 over monometallic catalysts with TiO_2 as the carrier were first compared at various conditions

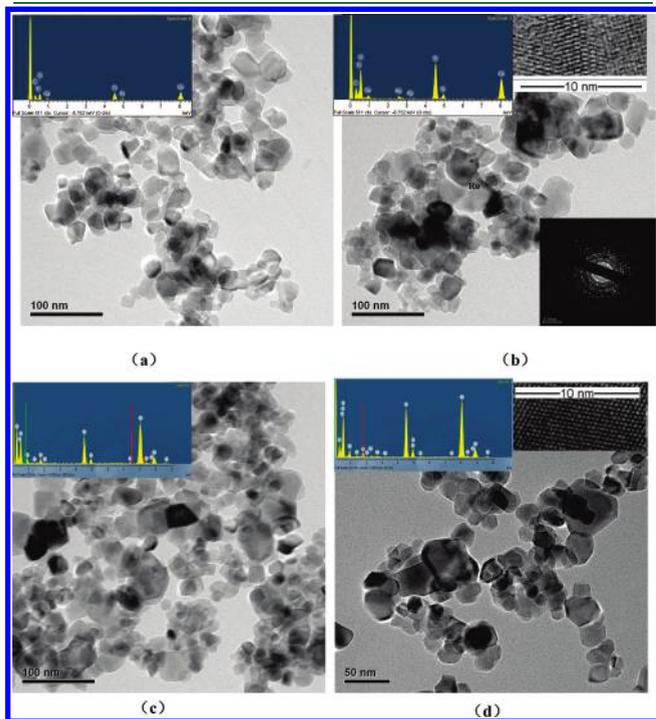


Figure 1. TEM micrographs, SAED patterns and EDX of (a) TiO_2 , (b) Ru/TiO_2 , (c) SCR_2 ($\text{V-W}/\text{TiO}_2$) and (d) Ru/SCR_2 .

(Figure S3 in SI). Among the tested catalysts with TiO_2 as the carriers, Ru/TiO_2 catalyst displayed remarkable promotion to Hg^0 oxidation among the tested catalysts even at 423 K, which indicated that RuO_2 showed better catalytic activity at lower temperature. Though the catalytic activities of some transition metals (e.g., Mn/TiO_2 and Cu/TiO_2) appeared to be very sensitive to SO_2 , the effect was relatively slight for Ru/TiO_2 and Hg^0 conversion was remained at about 85% in the presence of 500 ppm SO_2 , with a drop of about 9% at 623 K. Therefore, it has been clearly demonstrated that Ru was an efficient element for the catalytic oxidation of Hg^0 .

RuO_2 Modified SCR Catalyst. In order to make good use of SCR catalyst for the cobenefit of Hg^0 oxidation, RuO_2 was used as the dopant to SCR and its related catalysts. For the conventional SCR catalyst, V_2O_5 and WO_3 are the principal catalytic compositions with TiO_2 as the carrier. The interactions of RuO_2 with these elements for the catalysis were investigated, and the results are shown in Figure 2. The Hg^0 conversion efficiency over $\text{V-W}/\text{TiO}_2(\text{SCR}_1)$ and the commercial catalyst (SCR_2) were close to each other, which were less than the results in the literature¹⁶ because much higher space velocity was employed in this study. Meanwhile, Hg^0 conversion over V/TiO_2 catalyst was also close to that over SCR_1 or SCR_2 , but W/TiO_2 catalyst showed less activity to Hg^0 oxidation. Thus V_2O_5 was considered to be the main active component to Hg^0 conversion in SCR catalyst. However, the different content of V_2O_5 in SCR_1 (about 1%) and SCR_2 (0.52%) did not result in a remarkable difference in Hg^0 conversion.

Although SCR and its related catalysts were less effective at low HCl concentration, $\text{Ru-V-W}/\text{TiO}_2$ (Ru/SCR_1) and Ru/SCR_2 displayed rather high activities to Hg^0 oxidation. Both can obtain over 95% of Hg^0 oxidation efficiencies at 623 K without SO_2 . Meanwhile, both the catalysts displayed excellent tolerance to SO_2 for Hg^0 oxidation compared with Ru/TiO_2 , and Hg^0 oxidation efficiency drop only about 3–5% in the presence of 500 ppm SO_2 .

Effect of Ru Loading Content and HCl Concentration on Hg^0 Conversion. The effect of RuO_2 loading amount on Hg^0 oxidation was determined. As shown in Figure 3, the oxidation efficiencies of Hg^0 rise with the increase of RuO_2 loading on TiO_2 , and the increasing trend of Hg^0 oxidation efficiencies was

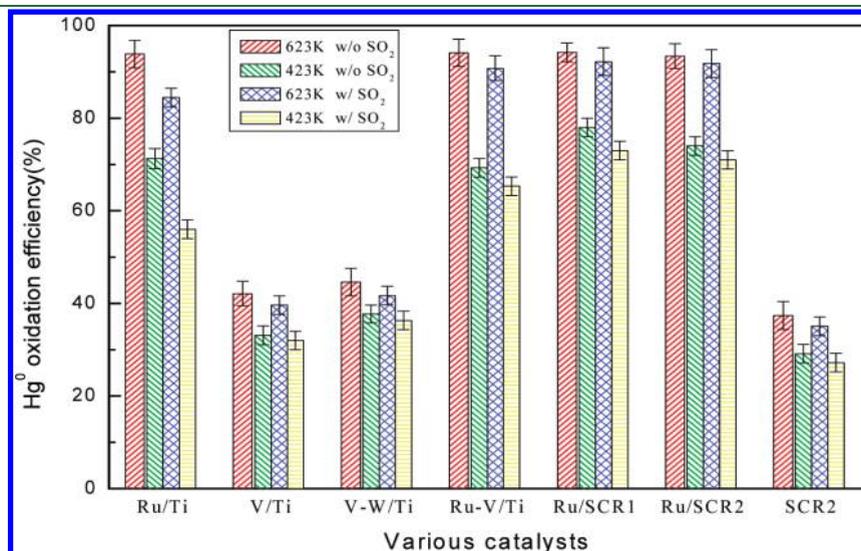


Figure 2. Comparison of the Hg^0 catalytic oxidation efficiencies over various multimetallic TiO_2 -supported catalysts and SCR catalyst with 5 ppm HCl.

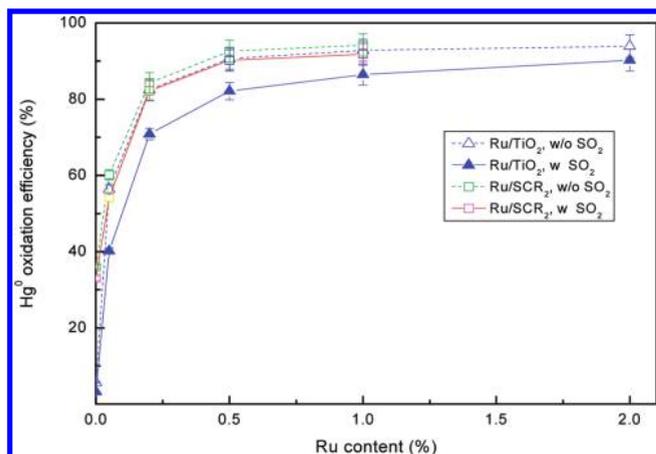


Figure 3. Effect of Ru loading on TiO₂ and SCR catalysts on the Hg⁰ oxidation efficiency at 623K and 5 ppm HCl.

more remarkable as it rise from 0.05% to 0.5%. Then it tended to be flat when the Ru loading increased from 0.5% to 2%. As for the RuO₂ modified SCR catalysts, Hg⁰ conversion increased from about 37% to 57% with 0.05% of Ru addition in the presence of 500 ppm SO₂ and 5 ppm HCl at 623 K, and it was about 84% and 90% with 0.2% and 0.5% of Ru, respectively. Considering on the consumption of Ru and the enhancement of Hg⁰ conversion, the optimal Ru content in SCR was at about 0.5%.

The effects of HCl concentration on Hg⁰ conversion over Ru/TiO₂ and Ru/SCR₂ catalyst are shown in Figure 4. With the increase of HCl concentration from 2 ppm to 12 ppm, Hg⁰ oxidation efficiency went up accordingly, and it became flat as the HCl concentration was above 5 ppm at 623K. Hg⁰ oxidation efficiency over Ru/SCR₂ catalyst (1% of Ru) was more than 90% with only about 5 ppm HCl. However, Hg⁰ oxidation efficiency over the original SCR catalyst was just about 47% even with more than 10 ppm HCl, which was even less than that with 2 ppm HCl on Ru/SCR₂. Therefore, Ru/SCR is very suitable for the catalyst oxidation of Hg⁰ in flue gas with low level HCl from low-chlorine coal utilization.

Effect of Various Gaseous Components on Hg⁰ Conversion. In addition to SO₂, the effects of other gaseous components on Hg⁰ oxidation over various catalysts were also evaluated (Figure S4 in SI). It was found that NO itself displayed a slightly promotional effect on Hg⁰ oxidation over the catalysts (with the increase of 2–5%), which is consistent with the similar research.¹³ The presence of water vapor (4%) did not show significant effect on Hg⁰ oxidation at 623 K. Hg⁰ conversion in the simulated flue gas with various components decreased slightly due to the inhibition of SO₂ (about 1–4% of the drop)

However, the presence of NH₃ showed obvious inhibition on the Hg⁰ oxidation by HCl (Figure 5). It was observed that NH₃ can strongly compete with Hg⁰ to adsorb on the catalyst in the absence of HCl. Even with 5 ppm HCl, Hg⁰ conversion sharply dropped to only about 15% over Ru/SCR₂ if 260 ppm NH₃ presented in the gas. Interestingly, the coexistence of NO with NH₃ can significantly mitigate such inhibition, and Hg⁰ conversion efficiency recovered to 65% with 300 ppm NO and 260 ppm NH₃ in the gas. Moreover, Ru/SCR₂ showed better NH₃ tolerance than Ru/TiO₂ for Hg⁰ conversion, which can be tentatively attributed the effective consumption of NH₃ through NO reduction over SCR catalysts. In addition, the Hg⁰ oxidation efficiency over Ru/SCR₂ was still as high as 90% if 30 ppm NO

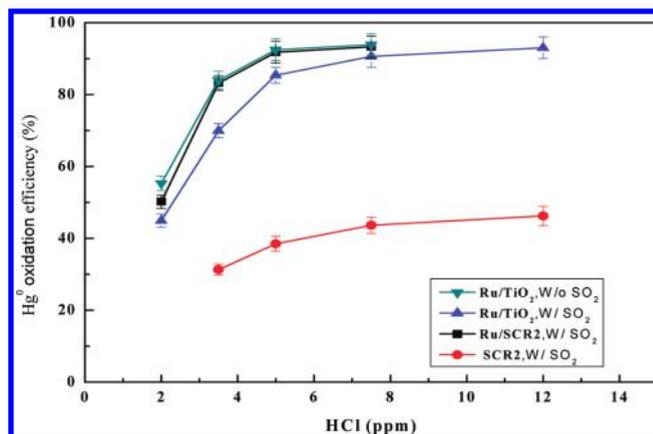


Figure 4. Dependence of Hg⁰ oxidation efficiencies on HCl concentration over Ru/TiO₂ and Ru/SCR catalysts at 623 K.

and 30 ppm NH₃ were presented, respectively. Therefore, the downstream section of SCR catalyst appeared to be more effective to Hg⁰ conversion as NH₃ concentration decreased, and Ru modified catalyst can be installed at the tail section of the SCR.

Effect of RuO₂ on NO Reduction and SO₂ Oxidation. In addition, the effect of the RuO₂ on NO reduction over the modified SCR₂ catalysts were also investigated (Figure S5 in SI). It was found the presence of RuO₂ in the catalysts did not show obvious effect on NO conversion by the comparison of the catalysts with and without RuO₂. Therefore, RuO₂ appeared to be well cooperative to SCR catalyst for Hg⁰ conversion.

The oxidation degree of SO₂ to SO₃ over SCR catalysts is always an important concern because of the negative effect SO₃ on catalyst and smoke opacity.²¹ The conversion of SO₂ across SCR₂, Ru/SCR₂ catalysts were measured, and it was found that both SCR₂ and Ru/SCR₂ showed imperceptible effect on SO₃ formation in the tested condition (Figure S6 in SI, both within 1% of SO₂ conversion), which indicated that RuO₂ showed a good catalytic selectivity for Hg⁰ conversion. Therefore, the side-effect of RuO₂ employed in SCR catalysts was negligible on NO reduction and SO₃ formation

Catalytic Mechanism of RuO₂ to Hg⁰ Conversion TPR Performance. The temperature program reduction (TPR) by hydrogen of SCR₂, Ru/TiO₂ and Ru/SCR₂ catalysts were tested (Figure S7 in SI). For SCR₂, the peaks at about 510 and 820 °C corresponded to the reduction of V⁵⁺-V³⁺ and W⁶⁺-W⁰, respectively. The peak of Ru⁴⁺-Ru⁰ for Ru/Ti catalyst was at about 150 °C. However, the peak of Ru⁴⁺-Ru⁰ and V⁵⁺-V³⁺ shifted to 240 and 290 °C with the overlap, which might implicate that Ru–V complex was formed on the catalysts. Thus the activity of V in catalyst was improved, and Ru then showed a better tolerance to SO₂. According to the tested TPR spectrum, the presence of RuO₂ can make the reduction of V₂O₅ more easily, which can be attributed to the hydrogen spillover behavior of Ru.

The TOF_{Hg⁰} parameter catalyst turnover frequency (TOF_{Hg⁰}) is a basic parameter to evaluate catalyst's activities.²² Equation 1 can be used to calculate the TOF_{Hg⁰}.

$$\text{TOF}_{\text{Hg}^0} = \frac{\text{converted Hg}^0 \text{ per-minute (mole/min)}}{\text{ruover the catalyst (mole)}} \quad (1)$$

It was obvious that TOF_{Hg⁰} decreased with Ru content doped in the catalyst (Figure S8 in SI). For Ru/TiO₂, it was 19.5×10^{-5} and $2.3 \times 10^{-5} \text{ min}^{-1}$ for 0.2% and 2% of Ru content (without SO₂),

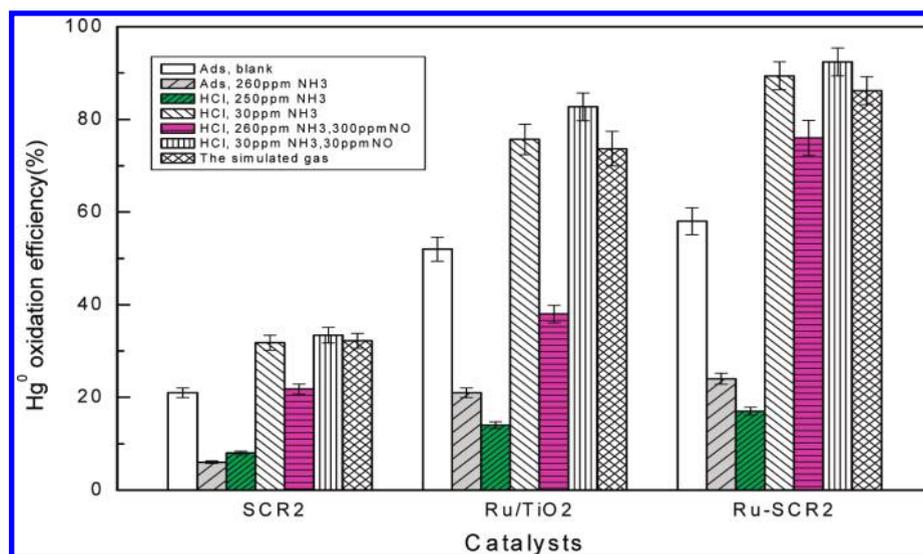


Figure 5. Effect of ammonia on Hg⁰ adsorption and conversion over SCR₂, Ru/TiO₂ and Ru/SCR₂ catalysts with various cases at 623 K.

respectively. The results implicated that Ru was well dispersed on the catalyst at low Ru content and most active sites can participate in the reaction. However, RuO₂ would aggregate to form larger particles with the increase of Ru content. The existence of V in the catalyst was helpful to Ru to keep its high TOF_{Hg⁰}, and the drop of TOF_{Hg⁰} for Ru/SCR₂ (1% of Ru) was only about 2% versus about 10% for Ru/TiO₂ in the presence of 500 ppm SO₂.

Ru Involved Deacon Reaction. As mentioned above, Deacon reaction might be the main pathway for Hg⁰ catalytic oxidation even though it has not been well understood yet.^{7,10} Therefore, the performance of Deacon reaction of RuO₂/TiO₂, Ru/SCR₂ and MnO_x/TiO₂ were preliminarily evaluated according to the yield of chlorine in this study. As shown in Figure 6, the yield of Cl₂ by Ru/TiO₂ catalyst was about 5 times higher than that with Mn/TiO₂, which indicated that RuO₂ was more effective than MnO_x for Cl₂ production. Meanwhile, the production of Cl₂ over Ru/SCR₂ was about 50% higher than that by Ru/TiO₂, in which V and/or W appeared to be synergetic with RuO₂ for the Deacon reaction.

In addition, the production of Cl₂ can be totally inhibited in the presence of 500 ppm SO₂ for all catalysts. Mn/TiO₂ almost lost all its activity to produce Cl₂ after contacting with SO₂ for 3 h. The produced Cl₂ by Ru/SCR₂ were nearly fully recoverable when SO₂ was removed from the gas, but it was with a loss about 60% for Ru/TiO₂. So V and/or W were believed to be helpful to improve the sulfur tolerance of Ru/SCR catalysts.

The reason why Ru/TiO₂ displays higher activity to Deacon reaction can be explained from the difference of the possible reaction mechanisms among the catalysts. As indicated in the previous research,^{20,21} Deacon reaction over RuO₂ catalyst was considered to be different from that on any transition metal oxides (e.g., MnO₂), and the conversion of HCl to Cl₂ can be occurred at the existing coordinative unsaturated sites over surface Ru atoms (cus-Ru), which will play an important role on Deacon reaction.

In addition, though it has been found that the production of Cl₂ was completely suppressed in the presence of SO₂ even for Ru/TiO₂ and Ru/SCR₂ catalyst, the Hg⁰ conversion efficiency still remained at about 90% in the presence of 500 ppm of SO₂. The results indicated that the production of Cl₂ was very

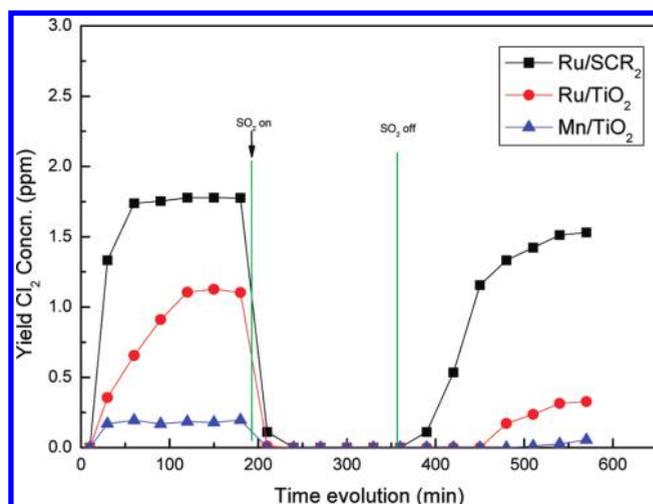
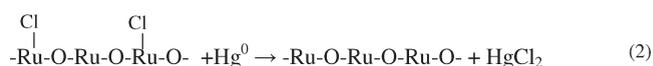


Figure 6. Cl₂ concentration produced by Deacon reaction over Mn/TiO₂, Ru/TiO₂, and Ru/SCR catalyst at 623 K.

sensitive to SO₂, and the combination reaction of atomic chlorines to form Cl₂ may be readily blocked by SO₂. In this situation, the catalytic oxidation of Hg⁰ over catalysts was just dependent on the atomic chlorines produced by the hydrogen abstraction reaction from HCl, which was still very effective for Hg⁰ oxidation and less sensitive to SO₂. The results also implicated that the partial Deacon reaction (to form atomic chlorine instead of Cl₂) was enough to oxidize Hg⁰.

Hg⁰ can be adsorbed on both virgin cus-Ru sites and then chlorinated by atomic chlorine on the near cus-Ru sites, and the gaseous Hg⁰ can even react with atomic chlorine directly.



As for the Ru/SCR₂ catalyst, it appeared to be less sensitive to SO₂. Though the production of Cl₂ was completely inhibited in the presence of SO₂, it can be fully recovered if SO₂ was excluded from the gas. Therefore, the presence of V and W in Ru-SCR

seemed to be helpful for Deacon reaction to the sulfur-resistance, which was consistent to its performance for Hg^0 conversion in the presence of SO_2 . The multimetallic centers over the catalyst might be favor to resist sulfur poison.

In addition, the XPS spectra of Ru ($\text{Ru}3d5/2$) indicates that Ru is in the form of RuO_2 (around at 280.8eV) on the catalysts (SI Figure S9). The XPS spectrum of $\text{Ru}3d5/2$ on Ru/TiO_2 after contacting with HCl and Hg^0 (in the absence of SO_2) almost remains the same as the fresh, which indicated that RuO_2 was stable to Deacon reaction and Hg^0 conversion reaction. The main spectrum of $\text{Ru}3d5$ in Ru/TiO_2 was observed to slightly shift to lower binding energy (about 0.15 eV) after contacting with SO_2 for 10 hrs. The spectrum of $\text{Ru}3d5$ for Ru/SCR_2 contacting with SO_2 remained almost the same with the fresh, which might implicate that RuO_2 on Ru/SCR_2 is more stable to SO_2 . Meanwhile, the spectrum of $\text{S}2p$ on Ru/TiO_2 was much stronger than that on Ru/SCR_2 , which indicated that SO_2 was more readily deposited to form sulfate on Ru/TiO_2 than that on Ru/SCR_2 . In summary, RuO_2 modified SCR catalyst appears to be very effective to Hg^0 conversion from coal-fired flue at high space velocity with low level of HCl, and only using small segment of the modified catalyst at the tail section of SCR may work efficiently for Hg^0 conversion, which deserves to the further demonstration in a large scale.

■ ASSOCIATED CONTENT

S Supporting Information. The typical mercury mass balance, ICP analysis, XRD patterns, the effect of various components, the conversion of NO and SO_2 , H_2 -TPR curves, turnover frequency, XPS analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

This study was supported by NSFC project (21077073) and the High-Tech R&D Program of China (863) under Grant No.2007AA06Z340. Thanks to Ms. Wenyang Zhang and Dr. Jiangkun Xie for the help with IC, ICP, XPS, and TEM analysis.

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