Novel Chlorination of Zirconium Dioxide at Low Temperature

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Low-temperature chlorination of zirconium dioxide using molybdenum pentachloride has been investigated below 773 K. The chlorination ratio was measured by chemical analysis, and the products were identified by powder X-ray diffraction. The results indicated that substitution of chlorine using molybdenum pentachloride significantly reduces the reaction temperature. Almost all the zirconium dioxide was converted to chloride in 30 minutes at 668 K when the molar ratio of molybdenum pentachloride to zirconium dioxide exceeded two. The chlorination reaction between zirconium dioxide and molybdenum pentachloride was shown to be a three-dimensional diffusion reaction satisfying the Jander equation, and the activation energy was 67 kJ/mole. Chlorination at a practical reaction rate using molybdenum pentachloride was realized at much lower reaction temperature than that using chlorine gas and carbon.

Key Words : Chlorination, Zirconium Dioxide, Molybdenum Pentachloride, Reaction Rate

1 Introduction

Chlorination is an important step in large-scale commercial zirconium refining. Zirconium chloride is then reduced by magnesium to yield zirconium metal. To minimize the energy consumption and the cost of chlorination facilities, various attempts have been examined to reduce the chlorination temperature¹⁾, and kinetics of the chlorination of zirconium dioxide (ZrO_2) by chlorine in the presence of a reducing agent has been reported.^{2,3)} The chlorination of ZrO_2 ¹⁻⁴⁾ and zirconium silicate^{5,6)} have been also studied by using several reducing agents, such as carbon, carbon monoxide or carbon tetrachloride.

The chlorination reaction of ZrO_2 can occur below 1000 K thermodynamically, but the reactions are only practical above 1000 K owing to the reaction rate.^{2,3)} The study of the chlorination reaction rate was reported to improve a carbon-metal oxide contact.²⁾ On the other hand, chlorine gas severely corrodes the container material, and the corrosion is accelerated at high temperatures.⁷⁾ The key issue of chlorination is to optimize the reaction temperature in consideration of reaction rate and the corrosion of the reactor vessel.

It is expected that the chlorination of ZrO_2 below 773 K reacts with a high reaction rate by using molybdenum pentachloride (MoCl_5); MoCl_5 simultaneously performs two roles: removing oxygen atoms and providing chlorine atoms. MoCl_5 should be in greater contact with ZrO_2 than carbon during chlorination, because MoCl_5 is a gas or liquid at the reaction temperature.

In this study, the chlorination reaction temperature between ZrO_2 and MoCl_5 was measured by thermal analysis, and then the chlorination reaction and reaction rate were determined by the isothermal reaction test. The chlorination of ZrO_2 by MoCl_5 was compared with the other chlorination of ZrO_2 at chlorination temperature and reaction rate.

2 Chlorination Process Between Zirconium Dioxide and Molybdenum Pentachloride

The chlorination of ZrO_2 by using MoCl_5 was evaluated the applicability of the process by the thermodynamic calculation and the difference of the vapor pressure as follows.

The Gibbs free energy changes of the chlorination reactions were calculated between ZrO_2 and MoCl_5 at 500 K by Malt-2⁸⁾. The thermodynamic data in Malt-2 had only molybdenum dichloride dioxide (MoO_2Cl_2) in molybdenum oxychlorides, and the reactions were evaluated between reactions (a) and (j) in Table 1. The chlorination reactions are possible to occur thermodynamically except the reactions (a), (e), and (g), and molybdenum tetrachloride (MoCl_4) production reactions (i) and (j) are predicted to occur more easily than the other reactions. $-\Delta G$ of gas MoCl_5 is larger than that of liquid MoCl_5 . Thus, the chlorination of ZrO_2 was considered to react with either of gaseous or liquid MoCl_5 in the sealed vessel.

Figure 1 shows the temperature variation of the vapor pressures of the related compounds.⁹⁻¹²⁾ The vapor pressure of MoO_2Cl_2 ⁹⁾ is three orders of magnitude higher than that of zirconium tetrachloride (ZrCl_4)¹⁰⁾. The vapor pressure of ZrCl_4 is much higher than that of the molybdenum production compounds (molybdenum dichloride (MoCl_2)⁸⁾, molybdenum trichloride (MoCl_3)⁸⁾, MoCl_4 ¹¹⁾, and molybdenum dioxide (MoO_2)¹²⁾). After chlorination, the molybdenum production compounds were considered to be separated from ZrCl_4 by the distillation.

When the regeneration reactions of molybdenum production compounds were evaluated thermodynamically between reactions (k) and (v) in Table 1, the molybdenum production compounds were considered to convert to MoCl_5 with the chlorine gas and carbon except reaction (p). MoCl_5 could be recycled as the chlorination reagent.

Table 1 Gibbs free energies changes of chlorination reaction and regenerated reaction at 500K.

No.	Chlorination reaction	ΔH (kJ/mole)	ΔG (kJ/mole)
(a)	$\text{ZrO}_2(\text{s}) + 4/5\text{MoCl}_5(\text{l}) = \text{ZrCl}_4(\text{s}) + 2/5\text{MoO}_2(\text{s}) + 2/5\text{MoO}_3(\text{s})$	-9.7	+14.7
(b)	$\text{ZrO}_2(\text{s}) + 4/5\text{MoCl}_5(\text{g}) = \text{ZrCl}_4(\text{s}) + 2/5\text{MoO}_2(\text{s}) + 2/5\text{MoO}_3(\text{s})$	-64.7	-1.3
(c)	$\text{ZrO}_2(\text{s}) + \text{MoCl}_5(\text{l}) = \text{ZrCl}_4(\text{s}) + 1/2\text{MoO}_2(\text{s}) + 1/2\text{MoO}_2\text{Cl}_2(\text{g})$	+11.0	-4.2
(d)	$\text{ZrO}_2(\text{s}) + \text{MoCl}_5(\text{g}) = \text{ZrCl}_4(\text{s}) + 1/2\text{MoO}_2(\text{s}) + 1/2\text{MoO}_2\text{Cl}_2(\text{g})$	-57.8	-24.3
(e)	$\text{ZrO}_2(\text{s}) + 4/3\text{MoCl}_5(\text{l}) = \text{ZrCl}_4(\text{s}) + 1/3\text{MoCl}_2(\text{s}) + \text{MoO}_2\text{Cl}_2(\text{g})$	+61.7	+4.7
(f)	$\text{ZrO}_2(\text{s}) + 4/3\text{MoCl}_5(\text{g}) = \text{ZrCl}_4(\text{s}) + 1/3\text{MoCl}_2(\text{s}) + \text{MoO}_2\text{Cl}_2(\text{g})$	-30.0	-22.0
(g)	$\text{ZrO}_2(\text{s}) + 3/2\text{MoCl}_5(\text{l}) = \text{ZrCl}_4(\text{s}) + 1/2\text{MoCl}_3(\text{s}) + \text{MoO}_2\text{Cl}_2(\text{g})$	+45.5	+2.5
(h)	$\text{ZrO}_2(\text{s}) + 3/2\text{MoCl}_5(\text{g}) = \text{ZrCl}_4(\text{s}) + 1/2\text{MoCl}_3(\text{s}) + \text{MoO}_2\text{Cl}_2(\text{g})$	-56.7	-24.7
(i)	$\text{ZrO}_2(\text{s}) + 2\text{MoCl}_5(\text{l}) = \text{ZrCl}_4(\text{s}) + \text{MoCl}_4(\text{s}) + \text{MoO}_2\text{Cl}_2(\text{g})$	+13.1	-42.9
(j)	$\text{ZrO}_2(\text{s}) + 2\text{MoCl}_5(\text{g}) = \text{ZrCl}_4(\text{s}) + \text{MoCl}_4(\text{s}) + \text{MoO}_2\text{Cl}_2(\text{g})$	-124.5	-83.0
No.	Regeneration reaction	ΔH (kJ/mole)	ΔG (kJ/mole)
(k)	$\text{MoCl}_2(\text{s}) + 3/2\text{Cl}_2 = \text{MoCl}_5(\text{l})$	-221.6	-144.6
(l)	$\text{MoCl}_2(\text{s}) + 3/2\text{Cl}_2 = \text{MoCl}_5(\text{g})$	-152.8	-124.5
(m)	$\text{MoCl}_3(\text{s}) + \text{Cl}_2 = \text{MoCl}_5(\text{l})$	-115.3	-91.8
(n)	$\text{MoCl}_3(\text{s}) + \text{Cl}_2 = \text{MoCl}_5(\text{g})$	-46.5	-71.8
(o)	$\text{MoCl}_4(\text{s}) + 1/2\text{Cl}_2 = \text{MoCl}_5(\text{l})$	-25.2	-0.6
(p)	$\text{MoCl}_4(\text{s}) + 1/2\text{Cl}_2 = \text{MoCl}_5(\text{g})$	+43.6	+19.5
(q)	$\text{MoO}_2\text{Cl}_2(\text{g}) + \text{C}(\text{s}) + 3/2\text{Cl}_2(\text{g}) = \text{MoCl}_5(\text{l}) + \text{CO}_2(\text{g})$	-303.2	-256.3
(r)	$\text{MoO}_2\text{Cl}_2(\text{g}) + \text{C}(\text{s}) + 3/2\text{Cl}_2(\text{g}) = \text{MoCl}_5(\text{g}) + \text{CO}_2(\text{g})$	-188.2	-157.8
(s)	$\text{MoO}_2(\text{s}) + \text{C}(\text{s}) + 5/2\text{Cl}_2(\text{g}) = \text{MoCl}_5(\text{l}) + \text{CO}_2(\text{g})$	-257.0	-177.8
(t)	$\text{MoO}_2(\text{s}) + \text{C}(\text{s}) + 5/2\text{Cl}_2(\text{g}) = \text{MoCl}_5(\text{g}) + \text{CO}_2(\text{g})$	-234.4	-236.3
(u)	$\text{MoO}_3(\text{s}) + 3/2\text{C}(\text{s}) + 5/2\text{Cl}_2(\text{g}) = \text{MoCl}_5(\text{l}) + 3/2\text{CO}_2(\text{g})$	-230.2	-222.4
(v)	$\text{MoO}_3(\text{s}) + 3/2\text{C}(\text{s}) + 5/2\text{Cl}_2(\text{g}) = \text{MoCl}_5(\text{g}) + 3/2\text{CO}_2(\text{g})$	-276.5	-313.6

s: solid state, l: liquid state, g: gas state

Fig. 1 Vapor pressures of ZrCl_4 , MoCl_2 , MoCl_3 , MoCl_4 , MoCl_5 , MoO_2Cl_2 , and MoO_2 .

3 Experimental

3.1 Reagents

MoCl_5 and ZrO_2 powders were purchased from Rare Metallic Co. The purity of MoCl_5 was greater than 99% and that of ZrO_2 was greater than 99.9%. ZrO_2 powders were dried to remove absorbed water at about 573 K for 5 hour in an argon atmosphere where oxygen and mois-

ture contents were less than 2 ppm. The sintered ZrO_2 which was a 1.5 mm diameter sphere had 5 wt% yttria, and was purchased from Nikato Co. MoO_2Cl_2 was purchased from Aldrich Co, and used the standard material of X-ray analysis.

To thermal analysis and isothermal reaction, the powder of chemicals was vacuum-sealed in Pyrex tube. 200 to 300 mg of mixtures between ZrO_2 and MoCl_5 were loaded into the tubes. Since MoCl_5 is deliquescent in air, the mixture and loading of samples were performed in an argon atmosphere where oxygen and moisture contents were less than 2 ppm. The molar ratio (R_{feed}) of MoCl_5 to ZrO_2 was adjusted, where the ratio R_{feed} is given by

$$R_{\text{feed}} = \frac{\text{moles of MoCl}_5}{\text{moles of ZrO}_2} \quad (1)$$

3.2 Thermal analysis

The apparatus for thermal analysis (DTA) are shown in Fig. 2. The ratio R_{feed} was adjusted to 1.1. The sealed tube was set in a radiation furnace as shown in Fig. 2 (b). A K-type thermocouple was inserted into a hollow at the bottom of the tube, as shown in Fig. 2 (a). Molybdenum trioxide was used as a reference material. The temperature difference (ΔT) between sample and reference was measured with increasing the temperature. The heating rate was 2 K/min. The samples were heated to approximately 673 K from room temperature, and two cycles of heating and cooling were performed.

3.3 Isothermal reaction

The chlorination of ZrO_2 powder by MoCl_5 was carried out in the sealed glass tube under isothermal condition

from 468 to 781 K. Powders of ZrO_2 and MoCl_5 were mixed with the ratio R_{feed} in the range of 0.2 to 4. The tubes were set in the furnace, and the samples were heated at fixed temperatures for several hours.

The sintered ZrO_2 was employed to measure the reaction rate corrected by the surface area. 2 or 3 of sintered ZrO_2 were placed in the Pyrex tube, and the ratio R_{feed} was adjusted to approximately 3 by adding 0.2 to 0.3 g MoCl_5 to the tube. The samples were heated at fixed temperatures for several hours.

Table 2 shows the experimental conditions for the isothermal chlorination reaction between MoCl_5 and ZrO_2 .

3.4 X-ray diffraction analysis

The samples before/after the chlorination were measured by X-ray diffractometer (Rigaku Co., RINT-2500V).

Fig. 2 Apparatus used for thermal analysis of the chlorination reaction between MoCl_5 and ZrO_2 .

The samples of the ratio $R_{\text{feed}} = 1.1$ were heated at 781 K for 20 hour. The sample removed from the tube in an argon atmosphere was set in an X-ray sample with polyethylene cover to protect it against oxidation and deliquescence. Another sample obtained under the same chlorination condition used to separate highly volatile compounds such as MoCl_5 , MoO_2Cl_2 and ZrCl_4 . The bottom of the tube was heated for 7 hour at about 760 K, and the volatile compounds condensed at the cooled top. The evaporated sample was taken from the top of the tube. The diffraction peaks were identified by reference to the Joint Committee of the Powder Diffraction Standards (JCPDS).¹³⁾

3.5 Chemical analysis

In this study, products formed by the reaction were assumed to include ZrO_2 , ZrCl_4 , MoO_2 , MoO_3 , MoCl_2 , MoCl_3 , MoCl_4 , MoCl_5 , molybdenum trichloride oxide (MoOCl_3), molybdenum tetrachloride oxide (MoOCl_4) and MoO_2Cl_2 . The sample used in the isothermal reaction experiment was chemically analyzed to quantify the chlorination ratio by the method shown in Fig. 3. The molybdenum compounds are difficult to identify by only chemical analysis. However, the zirconium compounds can be identified by dissolving the sample in water, because ZrCl_4 is soluble in water and ZrO_2 is insoluble in

Fig. 3 Flow chart used for the chemical analysis of samples.

Table 2 Isothermal reaction experimental conditions.

Run	Form of ZrO_2	R_{feed} (moles of MoCl_5 /moles of ZrO_2)	Temperature (K)	Time (hour)
1	Powder	0.2, 0.5, 1.5, 2.5, 5.3	468	91
2	Powder	0.2, 0.4, 0.6, 1.2, 2.3, 2.8, 4.1	571	17
3	Powder	0.1, 0.5, 0.6, 2.0, 2.6, 3.7	685	21
4	Powder	0.05, 0.15, 0.3, 0.4, 1.0, 1.1, 1.9, 3.0, 3.5	781	20
5	Powder	2.6	473	0.5, 1.0, 2.0, 7.7, 91
6	Powder	2.6	561	0.5, 2.2, 3.9, 7.8, 24
7	Powder	2.6	668	0.5, 1.0, 4.0, 7.6, 24
8	Powder	2.6	773	0.5, 1.0, 2.0, 4.2, 7.8, 24, 32
9	Sinter	2.3 - 3.0	640	0.3, 4.0, 7.8, 8.0, 16.4
10	Sinter	2.8 - 2.9	674	2.0, 2.5, 3.7, 6.3, 7.8
11	Sinter	2.5 - 3.1	723	0.3, 0.8, 1.0, 1.5, 2.0, 3.6, 5.0

water. The ratio of ZrCl_4 to ZrO_2 quantitatively indicated the effect of chlorinating ZrO_2 using MoCl_5 . After the reaction, the sample was removed from the glass tube, and after weighing the sample, it was dissolved in water. This solution was filtrated by $0.45\ \mu\text{m}$ filter, and the filtrate concentration was adjusted to 1 mole/liter by adding nitric acid solution. Since the residue was a mixture of ZrO_2 and molybdenum compounds, the residue dissolved in concentrated nitric acid, and the remaining residue was separated by filtrating. The residue after adding acid was considered to comprise only ZrO_2 , and after drying, the number of moles of Zr in the residue was obtained from its weight. The acid filtrate concentration was adjusted to 1 mole/liter by adding nitric acid solution. The amounts of zirconium in the two filtrates were measured by an inductively-coupled plasma-emission spectrometer (Shimadzu Co., ICP-1000).

The amounts of loaded ZrO_2 were almost agreement with that of detected ZrO_2 by the chemical analysis, however, the mass balance of ZrO_2 in some ampules was given between 60 and 80 %, because some samples remained in the separated glass tube at the seal. The chlorination ratio of zirconium dioxide (R_{react}) is given by the following equation:

$$R_{\text{react}} = \frac{\text{Zr in water soluble sample (mole)}}{(\text{Zr in water soluble sample} + \text{Zr in acid soluble sample} + \text{Zr of residue})(\text{mole})} \quad (\%). \quad (2)$$

4 Results and Discussion

4.1 Chlorination reaction temperature

Figure 4 shows the DTA curves of MoCl_5 and the sample (the ratio $R_{\text{feed}} = 1.1$). An endothermic reaction in Fig. 4 (a) occurred at approximately 470 K, which corresponds to the melting of MoCl_5 (mp: 463 K).¹⁴⁾ As shown in Fig. 4 (b), a similar endothermic reaction of sample occurred at the same temperature, and then an exothermic reaction occurred at approximately 500 K. Because both endothermic and exothermic peaks disappeared in the second cycle, the exothermic reaction in the first

Fig. 4 DTA curves of (a) MoCl_5 and (b) MoCl_5 and ZrO_2 (the ratio $R_{\text{feed}} = 1.1$).

cycle was irreversible. The exothermic chlorination reaction was the reactions (b), (d), (f), (g), and (j) of gaseous MoCl_5 in Table 1. These results were suggested that ZrO_2 reacted with MoCl_5 at approximately 500 K.

4.2 Identification of chlorination reaction

The X-ray diffraction patterns of the samples are shown in Fig. 5. As compared to the unreacted sample (Fig. 5 (b)), the MoCl_5 peaks of the reacted sample (Fig. 5 (c)) disappeared and the new appeared peaks were MoCl_4 peaks and then were identified with MoO_2Cl_2 peaks which were observed in Fig. 5 (a). The peaks in the evaporated sample observed MoO_2Cl_2 and ZrCl_4 , as shown in Fig. 5 (d). These results suggest that ZrCl_4 , MoCl_4 , and MoO_2Cl_2 were produced by the reaction between ZrO_2 and MoCl_5 .

In Run 1 to 4 in Table 2, the chlorination ratio of ZrO_2 (the R_{react}) was determined relative to the ratio R_{feed} by the chemical analysis. The relationship between the R_{react} of ZrO_2 and the ratio R_{feed} is shown in Fig. 6. The R_{react} of ZrO_2 increased with increasing the ratio R_{feed} up to the ratio $R_{\text{feed}} = 2$, and almost all the ZrO_2 was converted to ZrCl_4 at the ratio $R_{\text{feed}} \geq 2$. It was necessary for the ratio R_{feed} to exceed 2 to convert all the ZrO_2 to ZrCl_4 . The relationship between the R_{react} of ZrO_2 and the ratio R_{feed} showed the same trend at reaction temperatures from 468 to 781 K. It is suggested that ZrO_2 reacted with both gaseous and liquid MoCl_5 , of which boiling point is 543 K¹⁵⁾.

It was supposed that the chlorination of ZrO_2 by using MoCl_5 of gas or liquid proceeded as the following same reactions (3)-(9). The chlorination reaction between ZrO_2

Fig. 5 X-ray diffraction patterns of the compounds formed by the reaction between MoCl_5 and ZrO_2 at 781 K for 20 hour (ratio $R_{\text{feed}} = 1.1$). (a) MoO_2Cl_2 , (b) before reaction, (c) after reaction, (d) evaporated sample.

Fig. 6 Relationship between chlorination ratio of ZrO_2 and molar ratio R_{feed} of MoCl_5 to ZrO_2 . Samples of MoCl_5 and ZrO_2 were obtained after reaching temperatures of 468, 571, 685 and 781 K.

and MoCl_5 was analyzed on the basis of the following reactions.

The chlorination reaction of ZrO_2 by MoCl_5 was considered to be the reactions (7) and (8) by the chemical analysis, and was shown to be the reaction (7) by the X-ray analysis. These results were strongly suggested that ZrO_2 is chlorinated by MoCl_5 by the reaction (7) under the present condition.

4.3 Reaction rate of ZrO_2 chlorinated by MoCl_5

The reaction rate between ZrO_2 and MoCl_5 was measured by the sample of the ratio $R_{\text{feed}} = 2.6$ at 473, 561, 668 and 773 K. The relationship between the chlorination ratio of ZrO_2 and reaction time is shown in Fig. 7. Approximately 100 hour was required for the complete conversion at 473 K. However, the reaction finished within 0.5 hour at 668 K. The reaction time of the ZrO_2 chlorinated by MoCl_5 was shortening with the increase of the reaction temperature, as shown in Fig. 7. ZrO_2 reacted more actively with the gaseous MoCl_5 than with the liquid.

It was supposed that the chlorination reaction of ZrO_2 by MoCl_5 was the three-dimensional diffusion reaction, because the similar chlorination reaction of ZrO_2 by using CCl_4 was the three-dimensional diffusion reaction in the range of 650 to 675 K¹⁾. The three-dimensional dif-

Fig. 7 Relationship between the chlorination ratio of ZrO_2 and the reaction time at the temperatures of 473, 561, 668, and 773 K (the ratio $R_{\text{feed}} = 2.6$).

Fig. 8 Relationship between $[1-(1-X)^{1/3-2}]$ and t at reaction temperatures of 473, 561 and 668 K (the ratio $R_{\text{feed}} = 2.6$).

fusion reaction is given in Jander equation.¹⁶⁾

$$[1-(1-X)^{1/3-2}] = kt \quad (10)$$

where X = fraction of ZrO_2 reacted at time t

k = reaction rate constant.

The relationship between $[1-(1-X)^{1/3-2}]$ and t is shown in Fig. 8. Because the chlorination reaction of ZrO_2 by MoCl_5 obeyed the Jander equation in the temperature range of 473 to 668 K, it was considered that the reaction between ZrO_2 and MoCl_5 was a three-dimensional diffu-

sion reaction. The reaction rate constant was calculated from the slope of Fig. 8. The reaction rate constant of the ZrO_2 chlorinated by MoCl_5 was increased with the increase of the reaction temperature. The relationship between the reaction rate constant and the reciprocal of reaction temperature is shown in Fig. 9. The activation energy of reaction (7) was 67 kJ/mole.

4.4 Comparison with other chlorination reactions

Table 3 shows the activation energies of the several chlorination reactions. The activation energy of the reaction between ZrO_2 and MoCl_5 was smaller than that of the chlorination of ZrO_2 by using CCl_4 at same reaction temperature, and then was smaller than that of the other chlorination reactions using chlorine gas and carbon. The chlorination reaction between ZrO_2 and MoCl_5 reacted at the lowest chlorination temperature in Table 3.

In Run 9 to 11 in Table 2, the chlorination rate of the sintered ZrO_2 by using MoCl_5 was compared with that by using carbon and chlorine gas which was reported by Landsberg²⁾. The chlorination rates of ZrO_2 are summarized in Fig. 10. The chlorination rate was approximate-

ly $10 \text{ mg} \cdot \text{hour}^{-1} \cdot \text{cm}^{-2}$ at 1300 K when using chlorine gas, however, for chlorination using MoCl_5 the same chlorination rate was realized at only 700 K. Consequently it is suggested that chlorination using MoCl_5 has a practicable rate of reaction at lower temperature than that of chlorination using chlorine gas.

5 Conclusion

(1) The chlorination of ZrO_2 by MoCl_5 proceeded around 500K, and the reaction was completed in 30 min. at 668 K.

(2) To convert all the ZrO_2 to ZrCl_4 , the number of moles of MoCl_5 must be twice that of ZrO_2 . The chlorination reaction between ZrO_2 and MoCl_5 is described by the equation

Fig. 9 Relationship between reaction rate constant and reciprocal of reaction temperature (the ratio $R_{\text{feed}} = 2.6$).

Fig. 10 The relationship between the chlorination rate of ZrO_2 and chlorination temperature: The broken line presents the conversion of ZrO_2 to ZrCl_4 using chlorine gas and -325 mesh carbon²⁾, and solid squares represent the conversion of balls of ZrO_2 stabilized with Y_2O_3 to ZrCl_4 using MoCl_5 .

Table 3 Activation energies of the several chlorination reactions.

Chlorination reaction	ZrO_2	Reagent	Kinetics equation	Temperature (K)	Activation Energy (kJ/mole)	Reference
$\text{ZrO}_2 + \text{C} + \text{Cl}_2 = \text{ZrCl}_4 + \text{CO}_2$	Powder	$\text{C} + \text{Cl}_2$	$kt = 1 - (1-X)^{1/3}$	943-1103	231	4
	Powder	$\text{C} + \text{Cl}_2$	$kt = \ln(1-X)$	1400-1700	93	3
			$kt = (1 - (1-X)^{1/3})^2$	650-675	278	1
$\text{ZrO}_2 + \text{CCl}_4 = \text{ZrCl}_4 + \text{CO}_2$	Powder	CCl_4	$kt = 1 - (1-X)^{1/3}$	700-750	154	1
			$Kt = X$	775-825	54	1
			$kt = (1 - (1-X)^{1/3})^2$	473-683	67	This work

(3) The chlorination reaction between ZrO_2 and MoCl_5 is a three-dimensional diffusion reaction satisfying the Jander equation, and the activation energy is 67 kJ/mole. Chlorination of ZrO_2 at a practical reaction rate using MoCl_5 was realized at much lower reaction temperature than that using chlorine gas and carbon.

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