Improvement of thermal stability of alumina by addition of zirconia

Tatsuro Horiuchi [*], Yutaka Teshima, Toshihiko Osaki, Toyohiko Sugiyama, Kenzi Suzuki and Toshiaki Mori

National Industrial Research Institute of Nagoya, Hirate-cho, Kita-ku, Nagoya 462-8510, Japan
E-mail: horiuchi@nirin.go.jp

Received 20 June 1999; accepted 6 August 1999

To maintain a large surface area at elevated temperatures, zirconia was added to transition alumina. The addition of a small amount of zirconia resulted in a marked suppression of phase transformation from θ- to α-alumina. After heating at 1200 °C, ZrO_2-containing alumina exhibited a large surface area of 50 m^2/g. UV-VIS and XRD measurements indicated that zirconia existed in a high dispersion state after calcining at 800 °C. XPS measurement also showed that zirconia existed as monolayer. Zirconia monolayers are concluded to cover the alumina surface and the interaction between them may be the cause for the suppression of phase transformation and also for the maintenance of the large surface area at elevated temperatures. The interaction remains up to 1200 °C, therefore, θ phase remained at 1200 °C.

Keywords: alumina, surface area, phase transformation, zirconia, thermal stability

1. Introduction

The thermal stability of a catalyst including a catalyst support, which means the maintenance of a large surface area at elevated temperatures, is an important property, because some catalytic systems are operated under a high-temperature condition. The catalyst used in emission control of automobile exhaust gases, especially in the close-coupled converter for cold start emission [1], is the case for demanding high thermal stability. High-temperature catalytic combustion also requires catalyst materials with high thermal stability [2].

Owing to its large surface area of $>$100 m^2/g, γ-alumina is most widely used as a catalyst support. However, the surface area greatly decreases after heating at $>$1150 °C, accompanying phase transformation from γ- to α-alumina. Suppression of the phase transformation is, therefore, a possible way to maintain a large surface area of alumina. Two possible methods were reported for the suppression of phase transformation: one was the addition of other elements, such as Si, La, Ba, or Zr [3–6], and the other was to decrease the bulk density of alumina powders [7].

According to our previous study, among the oxides of Si, Zr, and Ti, the former two oxides suppressed the phase transformation of alumina and SiO_2 was the most effective. As a result, a large surface area was maintained at elevated temperatures [3]. However, our preliminary experiment showed that at elevated temperatures, supported precious metal particles became large more readily on silica than on alumina, which leads to inferiority of silica as a support for precious metals. There may also be a similar inferiority on alumina covered with silica. Therefore, this paper describes in a systematic fashion the effect of zirconia added to alumina on the maintenance of its large surface area.

2. Experimental

2.1. Addition of zirconia

A commercially obtainable θ-phase alumina (TM100; surface area 110 m^2/g, Taimei Chemicals Inc.) was impregnated with an aqueous solution of $ZrO(NO_3)_2 \cdot 2H_2O$ (Wako Chemicals Inc.), followed by drying at 110 °C overnight and subsequent calcination at 800 °C for 1 h. Another method was also tried by using zirconium acetate and alumina aerogel by supercritical drying of ethanol. Details of the method were described in our previous papers. Calcined samples were further heated at 1100, 1200, 1300, and 1400 °C for 1, 3, and 12 h. The amount of zirconia added, varying from 0.43 to 14.8 wt%, was determined by using an ICP instrument (ISM-7000, Seiko Instruments Inc.) after dissolving a sample in a teflon autoclave with 15 ml (1 : 1) sulfuric acid at 150 °C overnight.

2.2. Characterization

Nitrogen absorption measurement was carried out by using a Belsorp 36 (Nippon Bel Inc.) for the determination of surface area. The crystalline phase was identified by X-ray powder diffraction (XRD) using an MXP3 powder diffractometer (MAC Science Inc.) operated at 40 kV and 20 mA with a Cu tube. UV-VIS spectra were measured with a UV-VIS spectrophotometer (U3000, Hitachi Inc.) in the wavelength range from 190 to 400 nm. The absorbance was determined by the translucent method [8]. The XPS spectra for Zr 3d and Al 2p were measured with a Kratos XSAM-800 by using Al Kα radiation (1485.9 eV, 12 kV

---

[*] To whom correspondence should be addressed.

and 10 mA) for excitation. The calibration of binding energy was made on the basis of the binding energy for Al 2p, i.e., 74.3 eV. The Al 2p peak was well fitted by a Gaussian-type function.

3. Results

Figure 1 illustrates XRD patterns of aluminas with and without zirconia after calcination at 800 °C. The diffraction peaks assignable to θ-phase alumina were only observed for aluminas with the zirconia content <9.4 wt%. For the sample containing 12.2 wt% zirconia, an additional peak appeared at $2\theta = 30°$, which was assigned to (100) diffraction of tetragonal zirconia. The (100) peak was more manifest for the addition of 14.8 wt% zirconia.

Figure 2 summarizes the variation of the XRD pattern of alumina containing 9.4 wt% zirconia with the heating temperature. While θ-phase alumina was still a major crystalline phase below 1200 °C, it completely transformed to α-phase alumina at >1300 °C. Tetragonal-phase zirconia was better crystallized with the elevation of the heating temperature.

Figure 3 shows UV-VIS spectra for alumina with different amounts of zirconia calcined at 800 °C together with those of a 0.01 M ZrOCl$_2$ solution and bulk zirconia. In the present study, ZrO(NO$_3$)$_2$ was used instead of ZrOCl$_2$. However, it was difficult to measure UV-VIS absorption of ZrO(NO$_3$)$_2$, because a broad absorption due to NO$_3^-$ ions appeared in the range of the observed wavelength. This was the reason why UV-VIS absorption of ZrOCl$_2$ was measured. While for the ZrOCl$_2$ solution a single absorption was observed at 199 nm, three peaks appeared at 198, 218, and 233 nm for bulk zirconia. For ZrO$_2$-containing alumina, a broader peak appeared at 198 nm and an obvious shoulder was observed at 214 nm for alumina with 12.2 and 14.8 wt% zirconia.

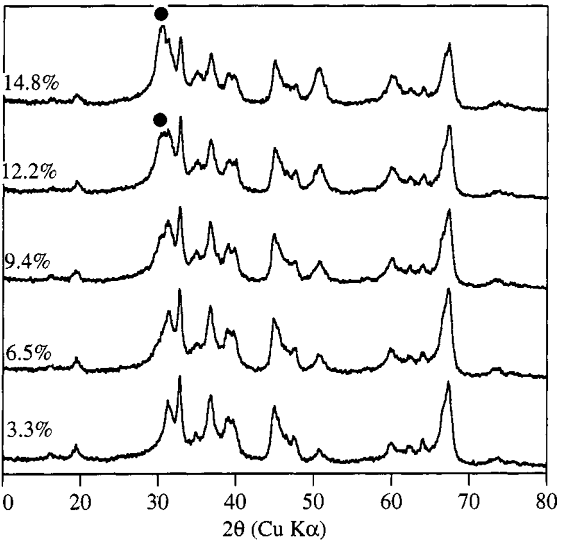


Figure 1. XRD patterns of zirconia-coated aluminas after heating at 800 °C. (●) Tetragonal-phase zirconia.

Figure 4 shows the XPS spectra of Zr 3d for alumina with 9.4 wt% zirconia varied with the heating temperature. In this figure, the intensity was normalized by dividing the peak height for Zr 3d by that for Al 2p. The doublet of Zr 3d$_{5/2}$ and 3d$_{3/2}$, which was typical for bulk zirconia, was clearly observed after heating at 1300 °C. For the calcination <1200 °C, the doublet was also obtained by the deconvolution of the observed complicated XPS signals. It is reported that when ZrO$_2$ is in a high dispersion state, Zr 3d peaks do not split into two peaks [9]. The larger peak was observed at 182.2 eV and the smaller one was 184.5 eV for all the heating temperatures. These binding

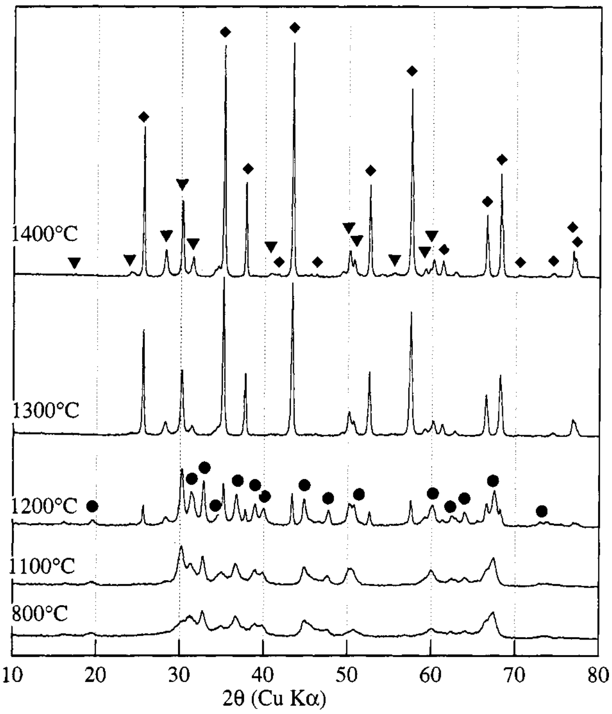


Figure 2. Change of XRD patterns of zirconia-coated alumina (zirconia 9.4%) with the heating temperature. (●) θ-phase alumina, (▼) tetragonal-phase zirconia, and (◆) α-phase alumina.

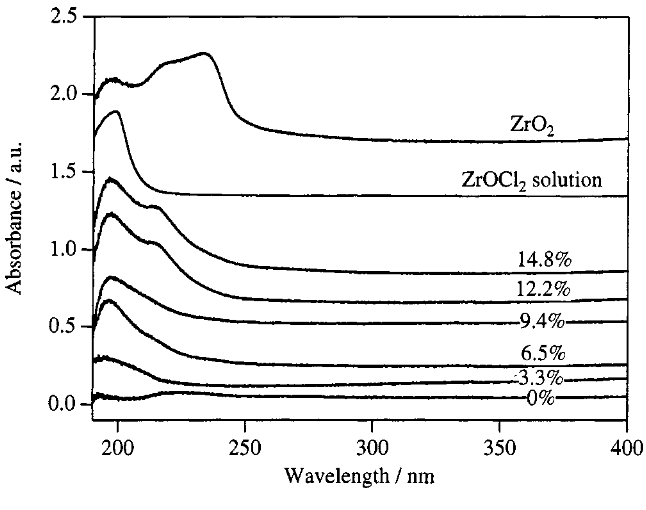
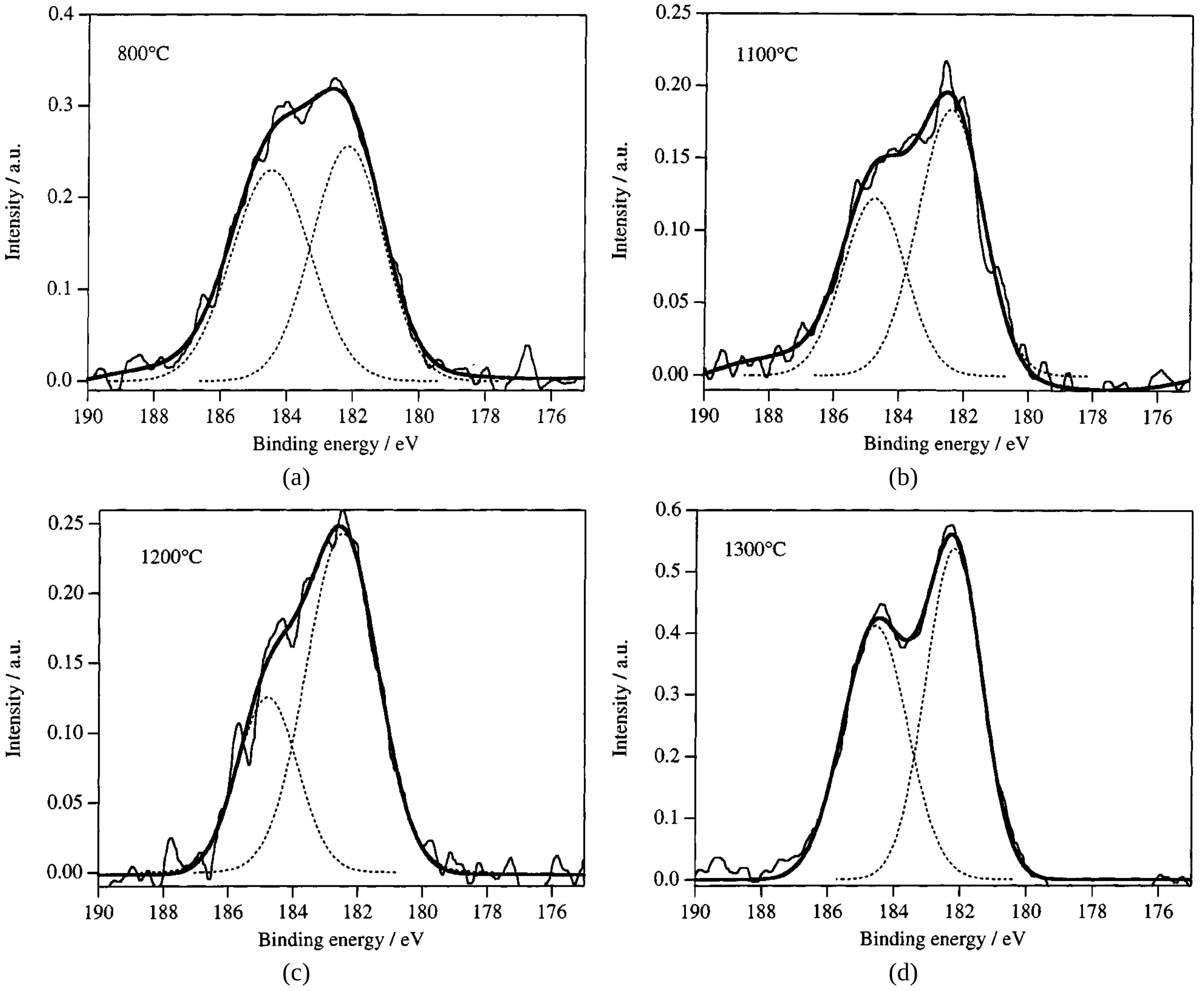


Figure 3. UV-VIS spectra of zirconia-coated aluminas.



(a) (b) (c) (d)

Figure 4. Change in the Zr 3d XPS spectra with the heating temperature of the samples with 9.4% zirconia: (a) 800, (b) 1100, (c) 1200, and (d) 1300 °C.

energies were quite similar to those of Zr $3d_{5/2}$ and $3d_{3/2}$ of ZrO_2.

Figure 5 illustrates the variation of the BET surface area with the amount of zirconia and the heating temperature. After heating at 1100 °C, the surface area was about 100 m^2/g irrespective of the amount of zirconia added, although it was slightly smaller for the addition of 0 or 0.43 wt% zirconia. After heating at 1200 °C, while the surface area was <10 m^2/g without zirconia, the addition of zirconia resulted in the maintenance of the quite large surface area of 40–50 m^2/g. It is interesting to note that after heating at 1200 °C, the largest surface area was obtained for the addition of 0.43 wt% zirconia. However, the effect of zirconia on the maintenance of the large surface area of alumina was not sufficient after heating at 1300 and 1400 °C, although all ZrO_2-containing aluminas exhibited larger surface area than zirconia-free alumina.

Long time endurance was also tested. In table 1, surface area changes of aluminas synthesized by various methods with the zirconia content of 9.4 wt% are shown. After 3 h heating at 1200 °C, the surface area of TM100 alumina became less than 10 m^2/g. The surface area of the alumina

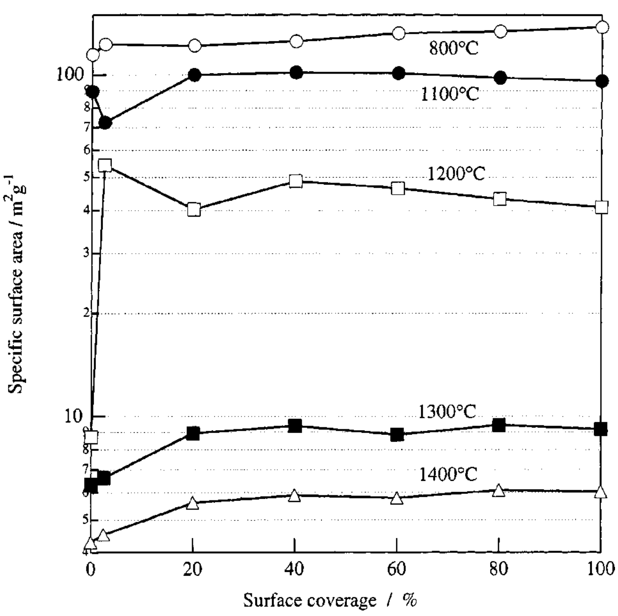


Figure 5. Change in BET surface area of zirconia-coated alumina with the heating temperature.

Table 1
BET surface area of various samples heated at 1200 °C for 3 and 12 h in air.

Sample	Specific surface area (m^2/g)	
	After 3 h	After 12 h
TM100 alumina	8.9	5.1
ZrO_2-coated Al_2O_3 from aerogel[a]	52.29	18.69
ZrO_2-coated Al_2O_3[b]	20.72	8.24

[a] ZrO_2 source: Zr acetate, ZrO_2 9.4 wt%.
[b] ZrO_2 source: $ZrO(NO_3)_2{\cdot}2H_2O$, ZrO_2 9.4 wt%.

by impregnation also decreased to 20 m^2/g and after 12 h heating its surface area decreased below 10 m^2/g. There is room for improving its long time durability. In order to improve the long time stability, a second method was tried. The sample synthesized by zirconia-containing alumina aerogel exhibited a higher surface area. After 12 h heating, its surface area was about 20 m^2/g. This method was better than the authentic impregnation method.

4. Discussion

For the $ZrOCl_2$ solution, a strong UV-VIS absorption appeared at 199 nm. It is reported that four zirconium atoms construct a hydrated complex ion, as shown in figure 6, in an aqueous solution of $ZrOCl_2{\cdot}8H_2O$ [10]. In this complex, each zirconium ion is located at the corner of a square plane and two of them are surrounded by two water molecules and six hydroxyl groups and the other two are surrounded by three water molecules and five hydroxyl groups. Such a structure of the complex ion is responsible for the UV-VIS absorption at 199 nm [11]. It was considered that the same complex ion was formed in $ZrO(NO_3)_2$ solution and the ions adsorbed or deposited on the alumina surface during impregnation were finally dehydrated to zirconia.

The absorption at 198 nm was also observed for all ZrO_2-containing aluminas calcined at 800 °C, which leads us to expect that a square plane complex-like structure was maintained on the alumina surface after calcination. However, compared with that of the $ZrOCl_2$ solution, the absorption peak of the zirconia on alumina was rather broad and a shoulder peak was also observed in the range of longer wavelength. Therefore, it should be concluded that an ill-crystallized bulky zirconia was dispersed on alumina after calcining at 800 °C, although the UV-VIS absorption peak at 233 nm, typical for bulk zirconia, was missing from the spectrum of zirconia on alumina. This conclusion was supported by XRD observation and XPS measurement for the sample calcined at 800 °C showing, respectively, no or very poor diffraction of zirconia and an ill-resolved doublet Zr 3d XPS peak.

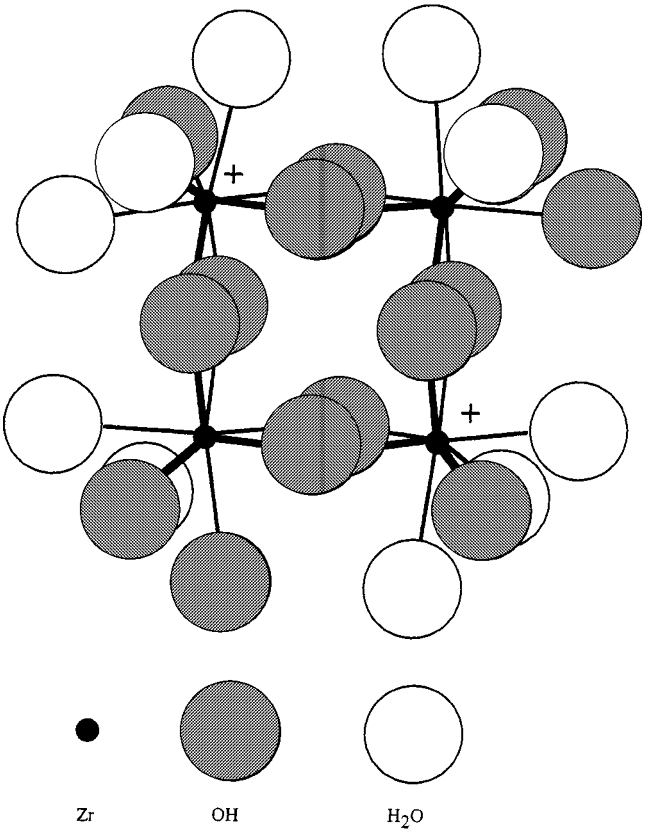


Figure 6. Schematics of $Zr_4(OH)_{14}(H_2O)_{10}^{2+}$ complex cation.

Since the lattice constant of cubic zirconia is 0.51 nm, the area of the (100) plane of the cubic zirconia unit cell, which is occupied by two zirconium atoms, is 0.26 nm^2. In other words, 1 g zirconia corresponds to an area of 635 m^2 monolayer. For the present samples with zirconia content of 0.43, 3.3, 6.5, 9.4, 12.2, and 14.8 wt%, the coverage with zirconia is calculated as 2.5, 20, 40, 60, 80, and 100%, respectively, by considering the surface area of alumina (110 m^2/g). On the other hand, according to XPS measurement, the thickness of thin zirconia layers was <3 nm. XRD also showed that for these samples, tetragonal zirconia was partly formed after calcination at 800 °C. It is, therefore, concluded that alumina is covered with a thin layer of zirconia.

In figure 7, the ratio of Zr 3d peak area to Al 2p peak area is plotted as a function of the Zr/Al atomic bulk composition ratio heated at 800 °C. As shown, the $I(\mathrm{Zr})/I(\mathrm{Al})$ ratio is proportional to the Zr/Al bulk composition ratio. Proportional parameter was used the photoelectron cross-sections by Scofield [12]. The linear relationship observed is understood in terms of the idea that a zirconia monolayer is formed [13,14]. An exception are the samples with 12.2 and 14.8 wt% zirconia. In these two samples, tetragonal zirconia peaks were observed. At temperatures >1100 °C, it is considered that monolayers of zirconia are reconstructed to bulk zirconia owing to the promoted migration of zirconia units. The decrease of the surface area of alumina also results in the promotion of the reconstruction. The clear appearance of the tetragonal zirconia, as shown in figure 2, is the case.

Up to 1200 °C, phase transformation from θ- to α-alumina was considerably suppressed by adding zirconia. Concerning the XPS spectrum of zirconium, the splitting of Zr 3d into Zr $3d_{5/2}$ and $3d_{3/2}$ (182.2 and 184.6 eV, re-

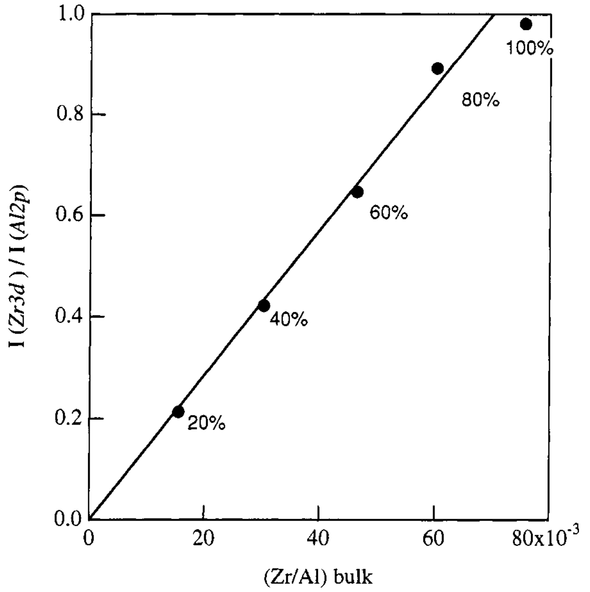


Figure 7. Relationship between the bulk atomic composition ratio of Zr/Al content and I(Zr 3d)/I(Al 2p).

spectively) is usually observed in its oxide state. In the present case, however, the splitting was opaque except for heating at 1300 °C. After heating at 1200 °C, the splitting was still opaque in spite of the formation of tetragonal zirconia. Although the phase diagram does not indicate the formation of any compounds between them, there may be interaction between alumina and zirconia and as a result, a considerable part of zirconia remained as thin raft-like layers. Such interaction may also be the cause for the suppression of phase transformation to α-alumina. After heating at 1300 °C, complete transformation to α-alumina and the splitting of the Zr 3d peak were observed, probably due to missing the interaction.

5. Conclusion

Phase transformation from θ- to α-alumina was suppressed by adding zirconia. After heating at 1200 °C, ZrO_2-containing alumina exhibited a surface area as large as 50 m^2/g. UV-VIS and XRD measurements indicated that zirconia existed in a very high dispersion state. XPS measurement showed that alumina was covered with a very thin monolayer of zirconia. The interaction between zirconia thin layer and alumina may be the cause for the suppression of the phase transformation of alumina.

References

[1] Z. Hu and R.M. Heck, SAE paper No. 950254 (1995).
[2] M. Machida, K. Eguchi and H. Arai, J. Catal. 103 (1987) 385.
[3] T. Horiuchi, T. Sugiyama and T. Mori, J. Mater. Chem. 3 (1993) 861.
[4] F. Oudet, P. Courtine and A. Vejux, J. Catal. 114 (1988) 112.
[5] M. Machida, K. Eguchi and H. Arai, Chem. Lett. (1987) 767.
[6] P. Burtin, J.P. Brunelle, M. Pijolat and M. Soustelle, Appl. Catal. 34 (1987) 225.
[7] T. Horiuchi, T. Osaki, T. Sugiyama, H. Masuda, M. Horio and T. Mori, J. Chem. Soc. Faraday Trans. 90 (1994) 2573.
[8] L.Y. Chen, S. Jaenicke, G.K. Chugh and H.G. Ang, J. Electron Spectrosc. Relat. Phenom. 82 (1996) 203.
[9] A.C.Q.M. Mejers, A.M. de Jong, L.M.P. van Gruijthuijsen and J.W. Niemantsverdriet, Appl. Catal. 70 (1991) 53.
[10] G.M. Much and P.A. Vaughan, J. Chem. Phys. 33 (1960) 194.
[11] S. Gontier and A. Tuel, Appl. Catal. A 143 (1996) 125.
[12] J.H. Scofield, J. Electron Spectrosc. Relat. Phenom. 8 (1976) 129.
[13] F.P.J.M. Kerkhof and J.A. Moulijn, J. Phys. Chem. 83 (1979) 1612.
[14] S. Dameyanova, P. Grange and B. Delmon, J. Catal. 168 (1997) 421.