Effects of transition metal promoters on the thermal stability of sulfated zirconia

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The effects of transition metal promoters on the thermal stability of sulfated zirconia (SZ) were studied by XRD and Raman spectroscopy. After calcination at 750 °C, the proportion of the monoclinic phase in SZ and 2.7 wt% Fe–SZ were 58 and 13%, respectively. Ni showed a smaller effect and Co showed a negative effect for the stabilization of the tetragonal phase. The results were compared with those of nonsulfated Fe-loaded zirconia, and it was suggested that Fe forms a solid solution with sulfated zirconia.

KEY WORDS: sulfated zirconia; Fe-promoted sulfated zirconia; monoclinic; tetragonal; thermal stability.

1. Introduction

Sulfated zirconia (SZ) is a solid superacid and is active for alkane isomerization even at room temperature [1,2]. Since it has stronger acidity than conventional solid acid catalysts such as zeolites, its application to a broad range of chemical processes that use acid catalysts is expected. It is known that the activity of sulfated zirconia for alkane isomerization is promoted by adding transition metals such as Fe or Mn. Hsu *et al.* reported that adding Fe–Mn to SZ increased the activity for *n*-butane isomerization by a factor of 10^3 [3]. Arata examined the effect of Mn, Fe, Co and nickel as promoters and showed that Fe had the highest promotion effect, Mn had a positive effect, while Co and nickel had negative effects.

The state of the Fe in Fe–SZ is still a matter of discussion. Scheithauer *et al.* examined Fe–SZ by ESR, Raman, XPS and TEM and concluded that Fe is present in an aggregated structure as Fe_2O_3 [4]. Tabora *et al.* concluded that Fe was not present in ZrO_2 crystallites and was present as Fe oxide clusters on the surface of ZrO_2 crystallites because their Fe–K EXAFS results did not show Fe–Zr and Fe–Fe peaks [5]. On the other hand, Yamamoto *et al.* concluded that Fe formed an interstitial-type solid solution with ZrO_2 based on characterizations by XAFS, X-ray diffraction (XRD), and Raman [6].

One of the significant problems in applying SZ is the deactivation caused by desorption or reduction of surface sulfates. Recently, the use of SZ as a catalyst support for envFemental catalysis is attracting attention [7–10]. Because exhaust treatment applications require long-term durability at high temperatures, the stability of SZ is particularly important. The author recently reported that adding Fe to SZ improved the durability of Pd–Pt/SZ catalyst for the selective reduction of nitrogen oxides with methane, and XRD of spent catalysts revealed that adding Fe suppressed the phase change from tetragonal to monoclinic [11]. In this paper, SZ and promoted SZ calcined at temperatures between 550–750 °C are examined by X-ray diffraction (XRD) and Raman, and the effects of promoters on the thermal stability of SZ are discussed. In addition, the state of Fe is discussed on the basis of the characterization results.

2. Experimental

2.1. Materials

Sulfated zirconia was prepared by immersing 180 g of zirconium hydroxide (79% as ZrO_2, Mitsuwa Chemical, Osaka) in a solution in which 27 g of ammonium sulfate (Hayashi Pure Chemicals, Osaka) was dissolved. After 15 h of impregnation, water was removed in an evaporator, and the solid was dried at 120 °C in an oven. The dried solid was calcined at different temperatures between 550–750 °C in flowing air. The temperature was raised from room temperature to the desired temperature over 6 h and kept at that temperature for 6 h. Transition metal-promoted SZ was prepared in a similar manner using $Fe_2(SO_4)_3 \cdot nH_2O$, ($n =$ ca. 15, Kanto Chemical, Tokyo), $CoSO_4 \cdot 7H_2O$ (Kanto Chemical), $NiSO_4 \cdot 6H_2O$ (Hayashi Pure Chemicals). For example, 0.75 wt% Fe–SZ was prepared using a solution in which 22.8 g of ammonium sulfate and 7.2 g of Fe sulfate hydrate were dissolved. The amount of ammonium sulfate was adjusted so that the nominal loading of sulfate equals that of SZ.

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For comparison, zirconia and Fe-loaded zirconia without sulfation were also prepared. Zirconia was obtained by calcining the zirconium hydroxide. Fe-loaded zirconia was prepared by impregnating zirconium hydroxide with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Hayashi Pure Chemicals). Calcination was carried out in a similar manner to that applied to SZ.

2.2. Characterization

The sulfur content of the sample was determined by ICP. The sample was treated with a 1 : 1 mixture of concentrated HCl and deionized water, and the sulfur in the solution was analyzed by ICP. The transition metal content of the promoted SZ was measured by X-ray fluorescence on a Rigaku RIX-3100 analyzer. BET surface area measurements were carried out using an automatic BET surface area analyzer (AMS-8000, Ohkura Riken, Tokyo). The amount of N_2 adsorption was measured at 77 K, $P/P_0 = 0.3$, and the surface area was calculated according to the one-point method.

XRD was measured with the Cu Kα radiation on a Shimadzu XRD-6100 diffractometer equipped with a graphite monochromator. The X-ray tube was operated at 40 kV and 40 mA. Both continuous-scan and step-scan measurements were carried out, the latter for quantitative analysis. A continuous-scan measurement was carried out between 15–80° at a rate of $3\,^\circ\,\text{min}^{-1}$. A step-scan measurement was carried out between 25–40° with a step of 0.02°, a dwelling time of 1.2 s and a rotation speed of 50 rpm. The phase compositions of zirconia were calculated according to the equation of Toraya *et al.* [12]. The crystallite size of the tetragonal zirconia was calculated according to the Scherrer's equation based on the line width of the (101) reflection of the tetragonal zirconia at $2\theta = 30.2^\circ$. The instrumental broadening was estimated to be 0.1° and was corrected.

A backscattered Raman signal was recorded on a Spex 1877 triple polychromator equipped with a liquid N_2-cooled CCD detector (Princeton Instruments, CCD-1752PBUV) at a spectral resolution of ca. $3\,\text{cm}^{-1}$. A 488-nm radiation from an Ar ion laser (Coherent, Innova 300) or a 532-nm radiation from an diode-pumped Nd : YAG laser (Coherent, DPSS 532-50) was used for excitation. A filter spectrometer (Spectrolab, Laserspec III) was used to eliminate plasma emission from the laser. The incident laser power was kept at less than 50 mW at the sample. All measurements were carried out under ambient conditions without any pretreatment of the samples. As a reference, α-Fe_2O_3 (99.97%, Kishida Chemicals, Osaka) was used.

3. Results

Table 1 shows the sulfur content of the samples. The sulfur content of SZ was 2.1 wt% after calcination at 550 °C. It decreased as the calcination temperature increased: 0.47 wt% after 650 °C calcination; 0.13 wt% after 750 °C calcination. Sarzanini *et al.* prepared SZ using ammonium sulfate and reported sulfur contents of 3.4 and 1.4 wt% after calcination at 550 and 650 °C, respectively [13]. Yamamoto *et al.* reported that the sulfur content was 0.88 wt% after calcination at 600 °C [6]. The difference may be caused by the difference in the zirconium hydroxide used for the preparation or in the calcination conditions, but the dependence on the calcination temperature is not much different. Since the nominal sulfur content is 4.1 wt%, about half of the loaded sulfate was lost after 550 °C calcination. The sulfur content of promoted SZ was higher than that of SZ, which suggests the stabilization of sulfate by these promoters. The sulfur content of Fe–SZ increased as Fe-loading increased. The sulfur content of 2.7 wt% Fe–SZ was 3.8 wt%, which is 90% of the nominal sulfur loading.

Table 1
Sulfur content (wt%)

Promoter	Calcination temperature (°C)				
	550	600	650	700	750
none	2.1	1.1	0.47	0.28	0.13
Fe 0.75 wt%	2.3	1.2	0.55	0.33	0.17
Fe 1.4 wt%	3.3	1.6	0.68	0.40	0.20
Fe 2.7 wt%	3.8	1.6	0.72	0.43	0.21
Co 1.1 wt%	2.5	1.2	0.59	0.36	0.15
Ni 1.2 wt%	2.5	1.2	0.60	0.38	0.15

Table 2 shows the BET surface areas of the SZ, promoted SZ, and Fe-loaded zirconia. The BET surface area of the 550 °C calcined SZ was $121\,\text{m}^2/\text{g}$, and the surface area decreased as calcination temperature increased. Sarzanini *et al.* reported surface areas of 154 and $115\,\text{m}^2/\text{g}$ for 550 and 650 °C calcined SZ. Yamamoto *et al.* reported a surface area of $98\,\text{m}^2/\text{g}$ for 600 °C calcined SZ. Our results are in agreement with previous reports. The surface areas of zirconia obtained by calcining zirconium hydroxide without sulfate treatment were much lower; the surface area of 550 °C calcined zirconia was $41\,\text{m}^2/\text{g}$. The effect of sulfate on the surface area is well known. The surface areas of Fe- or Ni-promoted SZ were higher than SZ, but the difference became small after 750 °C calcination. On the other hand, the surface area of Co-promoted SZ was smaller than SZ after calcination at 700 °C or higher. A similar effect of Fe on the surface area was also observed without sulfation.

Figure 1 shows the XRD of SZ and Fe-promoted SZ. SZ calcined at 550 °C showed strong peaks at $2\theta = 30$, 35, 50, and 60°. These peaks are assigned to the tetragonal zirconia. At higher calcination temperatures, peaks of the monoclinic phase appeared at $2\theta = 24$, 28° etc. Fe-promoted SZ also showed strong peaks at

Table 2
BET surface area (m^2/g)

Promoter	S loading (wt% nominal)	Calcination temperature (°C)				
		550	600	650	700	750
None	4.1	121	116	97	70	40
Fe 0.75 wt%	4.1	135	122	104	72	42
Fe 1.4 wt%	4.1	140	124	115	71	42
Fe 2.7 wt%	4.1	148	138	115	75	40
Co 1.1 wt%	4.1	128	126	93	60	21
Ni 1.2 wt%	4.1	129	122	96	65	29
None	0	41	30	23	17	17
Fe 0.86 wt%	0	49	33	29	23	22
Fe 1.6 wt%	0	55	40	29	23	19
Fe 3.2 wt%	0	57	42	32	25	19

$2\theta = 30$, 35, 50, and 60°, which indicates the tetragonal phase. Adding Fe suppressed the change to the monoclinic phase. While SZ and Fe–SZ with Fe contents up to 1.4 wt% completed crystallization at 550 °C, 2.7 wt% Fe–SZ did not complete crystallization at 550 °C as indicated by the weak diffraction lines and broad background in the XRD.

Figure 2 shows the XRD of zirconia and Fe-loaded zirconia calcined at 550–750 °C. Zirconia obtained by calcining zirconium hydroxide showed strong diffraction lines at $2\theta = 24$, 28, 31.5, 35, 50°, etc. These are assigned to the monoclinic phase. Samples calcined at 700 °C or lower temperatures showed a peak at $2\theta = 30.2°$ which is assigned to the tetragonal phase. Therefore, these samples contain the tetragonal phase as a minor component. The proportion of the tetragonal phase increased as the Fe content increased, although the major component was the monoclinic phase with an Fe content up to 1.6 wt%.

Figure 3 shows the proportion of the monoclinic phase, the crystallite size of the tetragonal phase and the diffraction angle of the (101) line of the tetragonal phase. Here, it should be noted that the diffraction angle is not corrected for any instrumental error. The error was estimated to be −0.05° at $2\theta = 30°$, and it was confirmed by the Si(111) diffraction line at $2\theta = 28.443°$. The proportion of the monoclinic phase was 58% in SZ calcined at 750 °C. Its value decreased as the Fe content increased. On the other hand, adding Fe affected the crystallite size little, which is in agreement with the BET results. Adding Co promoted the change to the monoclinic phase and the increase in the crystallite size. The diffraction angle of the tetragonal (101) line shifted to larger angles as the Fe content increased. The effect of adding Co or nickel on the diffraction angle was smaller than that of Fe.

Figure 4 shows the Raman spectra of SZ and Fe–SZ. SZ calcined at 550 °C was too fluorescent to obtain any usable spectrum. SZ calcined at 600 °C showed strong bands at 269, 317, 461, and 644 cm^{-1}. These are assigned to the tetragonal phase. Broadbands at 1030 and 1250 cm^{-1} are assigned to the sulfate group. Their

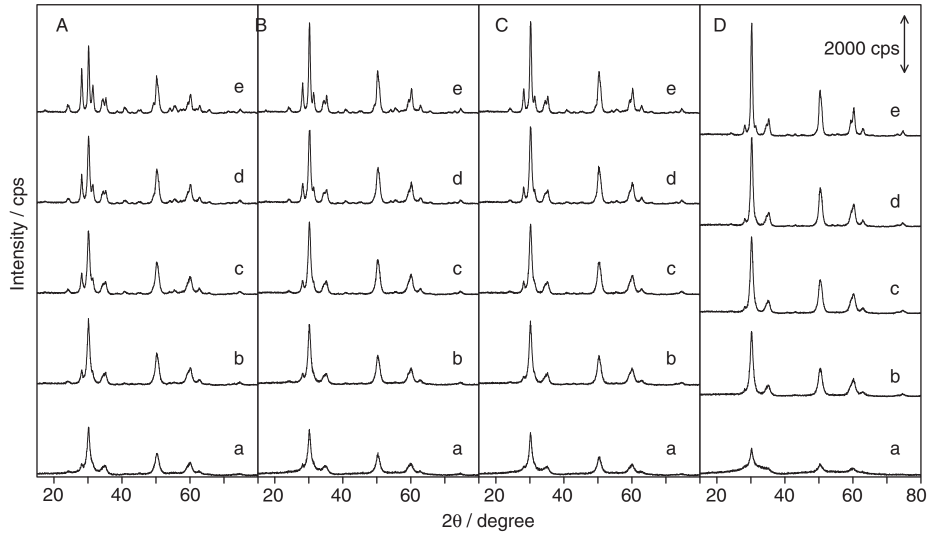

Figure 1. XRD of sulfated zirconia. Fe content: (A) 0, (B) 0.75 wt%, (C) 1.4 wt%, (D) 2.7 wt%. Calcination temperature: (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C, and (e) 750 °C.

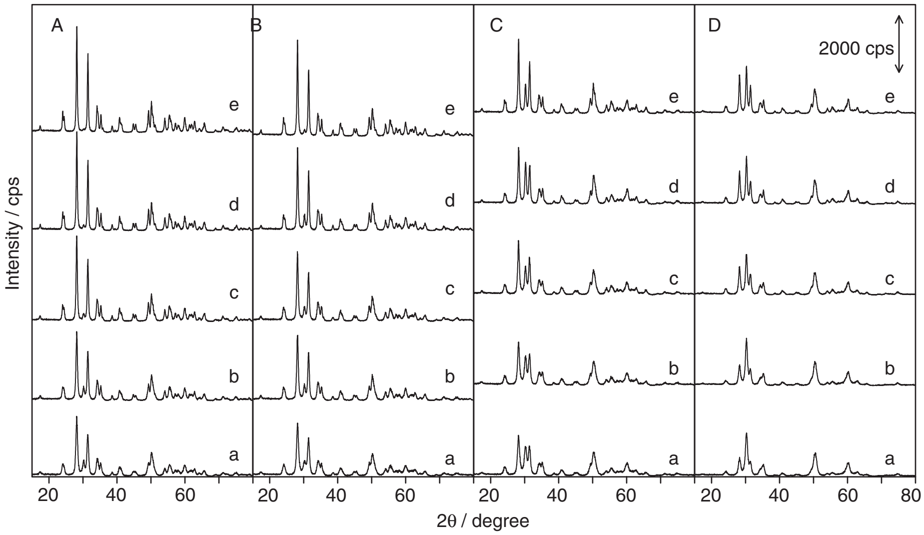

Figure 2. XRD of zirconia. Fe content: (A) 0, (B) 0.86 wt%, (C) 1.6 wt%, (D) 3.2 wt%. Calcination temperature: (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C, and (e) 750 °C.

intensities decreased with an increase in the calcination temperature, which is in agreement with the result of chemical analysis. By calcining at higher temperatures, the bands of the monoclinic phase appeared at 381 cm^{-1}, etc. Adding Fe suppressed the growth of the monoclinic phase. These are in agreement with the XRD results. Only 2.7 wt% Fe–SZ calcined at 550 °C showed a broadband centered at ca. 470 cm^{-1} in place of the bands of the tetragonal phase. Considering that the cubic zirconia showed a broadband at ca. 490 cm^{-1} [14], the Fe–SZ might be in the cubic form. While SZ showed two separate bands at ca. 1030 cm^{-1}, Fe–SZ showed only one band, which suggests the direct interaction of Fe and the sulfate. In the 488-nm excited Raman spectra of Fe–SZ, no band of Fe origin such as α-Fe_2O_3 was observed. Fe oxide (α-Fe_2O_3) shows strong bands at 224 and 290 cm^{-1}, and weaker bands at 406, 496, and 606 cm^{-1}, as well as a broadband at 1310 cm^{-1} (figure 5).

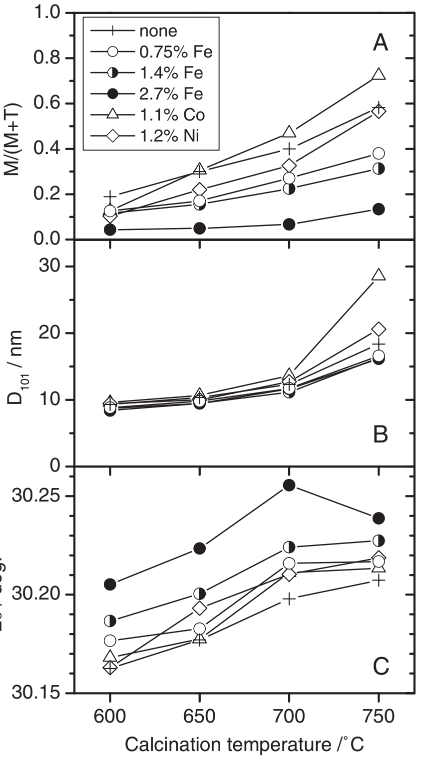

Figure 3. Change of (A) the proportion of the monoclinic phase, (B) the crystallite size of the tetragonal zirconia and (C) the diffraction angle (2θ) of the tetragonal (101) reflection with calcination temperature.

Figure 6 shows Raman spectra of zirconia and Fe-loaded zirconia. Zirconia showed sharp bands at 179, 191, 222, 306, 333, 347, 381, 475, 501, 537, 558, 614, and 636 cm^{-1}. These are assigned to the monoclinic phase. At a calcination temperature of 600 °C or lower, a small band is observed at 267 cm^{-1}, which is assigned to the tetragonal phase. The Raman spectra of 0.86 and 1.6 wt% Fe-loaded zirconia showed spectra similar to that of zirconia, but the bandwidths became broader. The band of the tetragonal phase at 269 cm^{-1} increased as the Fe content increased. It is difficult to determine whether 3.2 wt% Fe-loaded zirconia is tetragonal or monoclinic by Raman spectra, especially for those calcined at lower temperatures. In addition, 3.2 wt% Fe-loaded zirconia calcined at 550 °C showed a band of α-Fe_2O_3 at 407 cm^{-1}.

Figure 7 shows 532-nm excited Raman spectra of Fe–SZ and Fe-loaded zirconia. It has been reported that Fe–SZ showed strong absorption below 500 nm [4]. Accordingly, excitation at 488 nm gives rigorous resonance spectra, while excitation at 532 nm gives pre-resonance spectra. The improvement in signal-to-noise (S/N) ratio by 532-nm excitation is due to the weaker absorption of both incident and signal light by the samples. The 532-nm excited spectra of Fe–SZ did not clearly show bands of α-Fe_2O_3 either. On the other

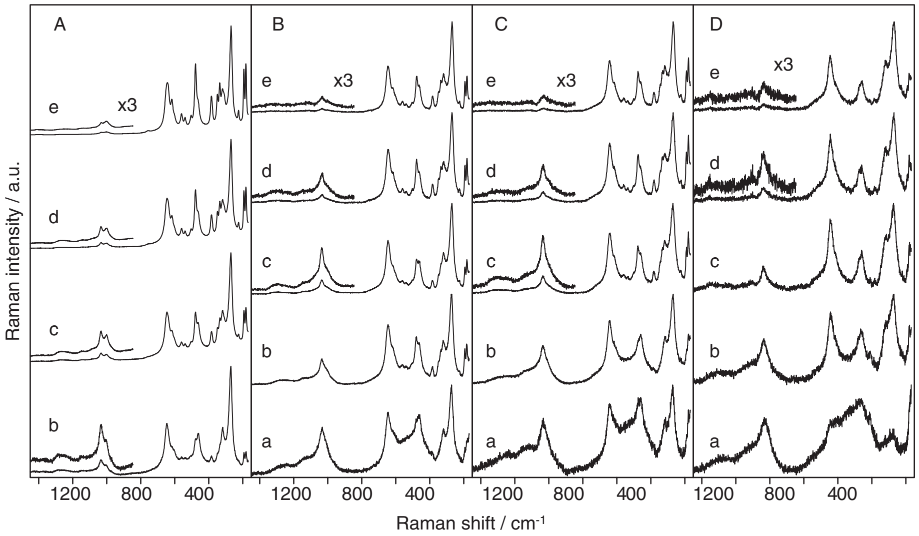

Figure 4. Raman spectra of sulfated zirconia. Fe content: (A) 0, (B) 0.75 wt%, (C) 1.4 wt%, (D) 2.7 wt%. Calcination temperature: (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C, and (e) 750 °C. Excitation wavelength: 488 nm.

hand, the spectra of Fe-loaded zirconia clearly showed bands of α-Fe_2O_3 at $406\,cm^{-1}$, regardless of the calcination temperature, which indicates the presence of α-Fe_2O_3 in these samples. It should be noted that the strongest band of α-Fe_2O_3 is at $224\,cm^{-1}$, and although the peak nearly coincides with the weak peak of monoclinic zirconia at $222\,cm^{-1}$, it becomes clear that the $224\,cm^{-1}$ bands in the spectra of 3.2 wt% Fe-loaded zirconia mainly came from α-Fe_2O_3, when the band intensities are compared with those of other bands of monoclinic zirconia. The difference in the appearance of the α-Fe_2O_3 bands was probably caused by different balances of intensity gain by the resonance effect and the intensity loss by absorption.

4. Discussion

Zirconia has three polymorphs: monoclinic, tetragonal, and cubic. Of these, the monoclinic phase is the stable phase below 1170 °C [15]. The tetragonal phase is the stable phase between 1170 and 2370 °C. SZ is tetragonal, and calcination at high temperatures causes loss of sulfate and transformation to the monoclinic phase [1]. Therefore, the tetragonal phase of SZ is considered to be stabilized by surface sulfate. The results of this study are in agreement with the previous study.

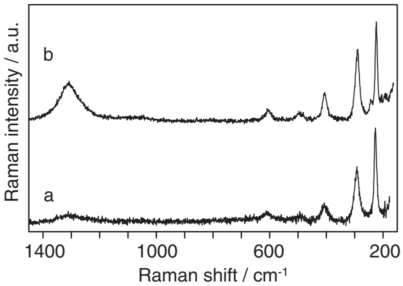

Figure 5. Raman spectra of α-Fe_2O_3. Excitation wavelength: (a) 488 nm and (b) 532 nm.

It is widely known that CaO, MgO, Y_2O_3, and CeO_2, etc., form solid solutions with zirconia and stabilize high temperature phases even at room temperature [15]. They are called *stabilized* or *partially stabilized zirconia*. There are few reports about the effects of Fe, Co and nickel. Stephanic *et al.* investigated Fe_2O_3–ZrO_2 with various compositions calcined at various temperatures by XRD and determined the solid solubility limits of Fe_2O_3 in ZrO_2 [16]. They concluded that the limit was 6.0 mol% at 500 °C and 4.0 mol% at 800 °C, and that adding Fe_2O_3 stabilized the cubic phase. Lajavardi *et al.* reported that $Fe_{0.1}Zr_{0.9}O_x$ was initially cubic, but transformed to tetragonal after 10 h and remained in this phase even after 45 h with no appearance of the monoclinic phase, when it was treated at 800 °C under Ar atmosphere [17]. They also observed the contraction of the lattice by adding Fe. They reported the following lattice parameters: $a = 0.5084\,nm$, $c = 0.5183\,nm$ for tetragonal zirconia; $a = 0.5073\,nm$, $c = 0.5178\,nm$ for $Fe_{0.1}Zr_{0.9}O_x$ (tetragonal). From these results, they concluded that Fe forms a substitutional-type solid solution with ZrO_2. When zirconium hydroxide is calcined, a metastable tetragonal phase appears before it turns into the monoclinic ZrO_2. The stability of the metastable phase depends on the preparation conditions of the zirconium hydroxide, but the transformation to the monoclinic phase usually completes at 550–600 °C [18–20]. Therefore, their results indicate the stabilization of tetragonal zirconia by forming a solid solution with Fe.

The Fe/Zr molar ratios of the samples used in this study were below the solubility limits reported in these previous studies. For example, it was 0.063 for 2.7 wt% Fe–SZ and was 0.074 for 3.2 wt% Fe-loaded zirconia. The (101) diffraction of tetragonal zirconia at $2\theta = 30.2°$

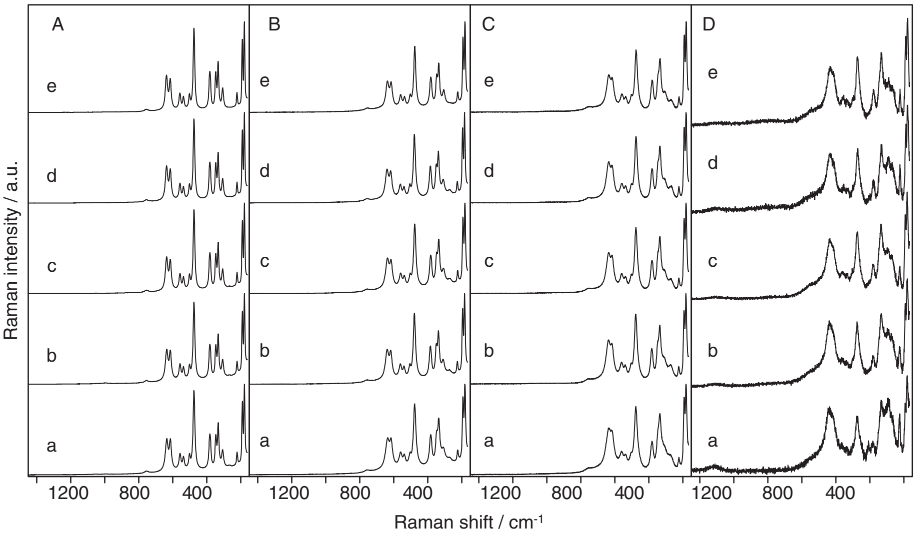

Figure 6. Raman spectra of zirconia. Fe content: (A) 0, (B) 0.86 wt%, (C) 1.6 wt%, (D) 3.2 wt%. Calcination temperature: (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C, and (e) 750 °C. Excitation wavelength: 488 nm.

shifted upward by 0.03–0.04° by adding 2.7 wt% Fe to SZ. The (−101) diffraction of monoclinic zirconia at $2\theta = 28.2°$ shifted upward by 0.05° by adding 3.2 wt% Fe to zirconia. The shift corresponds well with the value observed by Lajavardi *et al.* (0.05°) when the difference in the Fe/Zr ratio is taken into account.

The state of the Fe in Fe–SZ is still a matter of discussion. Yamamoto *et al.* examined 1.1 wt% Fe–SZ by XAFS and concluded that Fe formed an interstitial-type solid solution [6]. They prepared the Fe–SZ by treating zirconium hydroxide with ammonium sulfate followed by Fe impregnation using a solution of Fe nitrate. Scheithauer *et al.* examined 2 wt% Fe–SZ by Raman and electron microscopy and concluded that Fe is in an aggregated form as Fe_2O_3 [4]. They prepared their sample by impregnating a commercial sulfate-loaded zirconium hydroxide with an Fe nitrate solution. On the contrary, Fe_2O_3 was not clearly observed in Fe–SZ with Fe concentrations up to 2.7 wt% in this study. The different results may be caused by the different preparation methods. While both of Yamamoto *et al.* and Scheithauer *et al.* used stepwise impregnation, sulfate and Fe were impregnated simultaneously in this study. The drying after sulfate loading may have affected the formation of a solid solution, although the detailed condition is not reported. While Stefanic *et al.* and Lajavardi *et al.* could stabilize the cubic or the tetragonal phase by only Fe, 3.2 wt% Fe-loaded zirconia in this study consisted of both the tetragonal and the monoclinic phases, and at least some part of Fe was present as agglomerated α-Fe_2O_3. Both Stefanic *et al.* and Lajavardi *et al.* used coprecipitation. In contrast, Fe was loaded by impregnation on zirconium hydroxide in this study, which may have limited the formation of

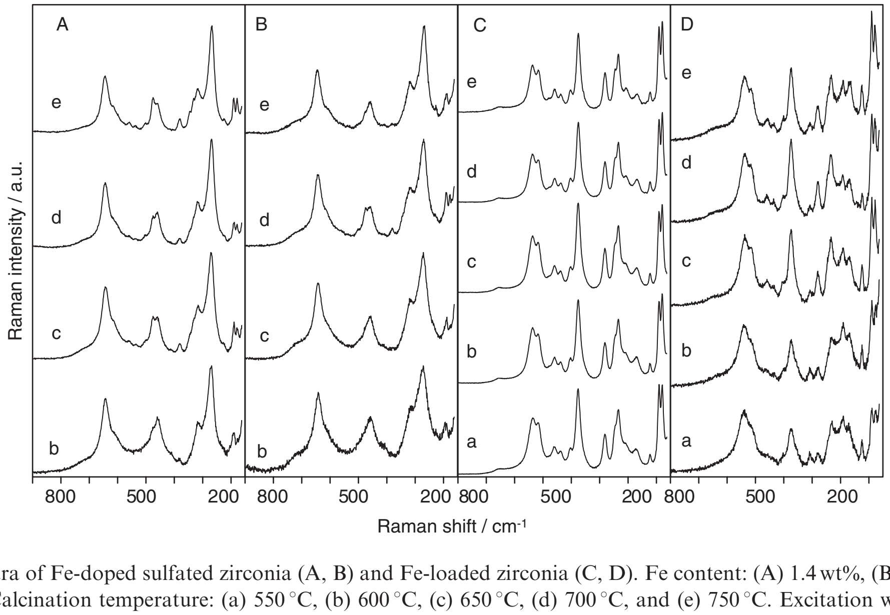

Figure 7. Raman spectra of Fe-doped sulfated zirconia (A, B) and Fe-loaded zirconia (C, D). Fe content: (A) 1.4 wt%, (B) 2.7 wt%, (C) 1.6 wt%, and (D) 3.2 wt%. Calcination temperature: (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C, and (e) 750 °C. Excitation wavelength: 532 nm.

solid solution near the surface of the zirconia crystallite and led to the incomplete stabilization.

There are only a few reports on adding nickel. Masteralo *et al.* showed by Fe–K and Ni–K EXAFS that in their CeO_2 (12 mol%)–ZrO_2 (88 mol%) system prepared by a solid-state method in which zirconia and ceria were calcined at 1450 °C, added Fe formed a solid solution with CeO_2–ZrO_2, while added Ni was in a form similar to NiO [21]. Lajavardi *et al.* examined the phase change of $Ni_{0.1}Zr_{0.9}O_x$ heated at 700 °C in air. It was cubic after 15 min, but the tetragonal phase appeared after 1 h, and the monoclinic phase became the main component (70%) after 90 h. From these results, they concluded that nickel is not a good stabilizer [17]. The results in this work showed stabilization but the effect was smaller than Fe, which is in agreement with the results of Lajavardi *et al.* The negative effect of Co was observed, but the reason is not clear at present.

To seek practical applications as acid catalysts, the effects of Fe on the acid sites should be clarified. At calcination temperatures of 700 °C or lower, adding Fe increased the sulfur content, which suggests that at least some part of Fe is present at the surface and interacts with the sulfate. The profile of the $1030\,cm^{-1}$ band of sulfate should be noted again. While it was a doublet in SZ, only one peak is observed in Fe–SZ. This fact also suggests a direct interaction of sulfate and Fe.

The loss of surface sulfate during reactions causes irreversible deactivation and is a major drawback of SZ compared with other solid acids such as zeolites. However, in exhaust treatment applications, the feed usually contains sulfur oxides at a level of 1–100 ppm. Therefore, the density of the surface sulfate may stabilize at a certain level at which adsorption and desorption reach equilibrium. This is only possible for Fe–SZ, because Fe–SZ remains tetragonal after the desorption of sulfate. SZ causes an irreversible change into the monoclinic phase and will not regenerate by readsorption of sulfates.

5. Conclusion

Adding Fe to SZ suppressed the change from the tetragonal phase to the monoclinic phase during calcination at high temperatures. Fe formed a solid solution with zirconia and stabilized the tetragonal phase. Ni showed a similar, but smaller effect, while Co promoted the transformation.

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