PREPARATION OF NiO-ZrO_2/SO_4^{-2} CATALYST AND ITS CATALYTIC ACTIVITY FOR ETHYLENE DIMERIZATION

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Abstract— NiO-ZrO_2/SO_4^{-2} catalysts were prepared by coprecipitation from the solution of nickel chloride - zirconium oxychloride mixture followed by treating with H_2SO_4. NiO-ZrO_2 alone without SO_4^{-2} was inactive as a catalyst for ethylene dimerization, but NiO-ZrO_2/SO_4^{-2} was found to be very active even at room temperature. The high catalytic activity of NiO-ZrO_2/SO_4^{-2} was closely correlated with the increase of acid strength by the inductive effect of sulfate ion adsorbed on NiO-ZrO_2. The decrease of catalytic activity above 450°C of evacuation temperature was explained in terms of the structural change of catalyst from amorphous phase to crystalline, and the sintering.

INTRODUCTION

Nickel oxides on silica or silica-alumina are effective catalyst in olefin dimerization and isomerization as well as in the hydrocracking, hydrogenation and methanation process following reduction of the nickel component [1-8]. One of the remarkable features of this catalysts system is its activity in the relation to a series of n-olefins. In contrast to usual acid-type catalysts, the nickel oxide on silica or silica-alumina shows a higher activity for a lower olefin dimerization, particularly for ethylene [1-5,9]. The catalyst is also active for the isomerization of n-butenes, the mechanism of which has been proved to be of a proton donor-acceptor type [10]. It was reported that the dimerization activities of such catalysts are related to the acid property of surface and low valent nickel ions. In fact nickel oxide which is active for C_2H_4-C_2D_4 equilibration acquires an activity for ethylene dimerization upon addition of nickel sulfate which is known to be an acid [11].

In the previous paper from this laboratory, it was reported that dimerization of ethylene to n-butenes preceeds selectively over nickel ion exchanged silicate, while chromium ion exchanged silicate is more effective for the polymerization of ethylene [12]. Recently, we found that the nickel oxide-titanium oxide treated with sulfate ion is very active for the dimerization reaction of ethylene at room temperature [13,14]. As an extention of studies on ethylene dimerization, these authors tried to prepare other catalyst systems by combining nickel hydroxide to give low valent nickel after decomposition, with ZrO_2 treated with H_2SO_4 which is known to be an acid [15]. In this way a new catalyst system of NiO-ZrO_2/SO_4^{-2} was found to be effective for the dimerization of olefins.

EXPERIMENTAL

Catalysts and Materials

The coprecipitate of $Ni(OH)_2$-$Zr(OH)_4$ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of nickel chloride and zirconium oxychloride at room temperature with stirring until the pH of mother liquor reached about 8. The ratio of nickel chloride to zirconium oxychloride was varied. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected, and was dried at room temperature. The dried precipitate was powdered below 100 mesh and then the treatment with sulfate ion was performed by pouring 30 ml H_2SO_4 into 2 g of the powdered sample on a filter paper and drying the sample in air. The dry solid powder was used as catalyst after decomposing at various evacuation temperature. Ethylene, propylene and 1-butene (99.95% pure) were obtained from Korea Petrochemical Industrial Co. and were purified by the freeze-thaw technique using liquid nitrogen and dry ice-acetone baths.

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Procedure

The catalytic activity for olefin dimerization was investigated at 20°C by a conventional static system, following pressure change from an initial pressure of 288 torr. Sometimes, the dimerization reaction was carried out in a circulation system at 185 torr in order to observe the variation of product distribution with reaction time. Each fresh catalyst of 0.2g was used for each run after evacuation to 10^{-4} torr at various evacuation temperature for 1.5 hr. The catalytic activity was evaluated as the amount of olefin consumed in the initial 5 minutes. Reaction products, which contain n-butenes isomers were analyzed by gas chromatography equipped with a VZ-7 column at room temperature. The measurement of the specific surface area were determined by adsorption of nitrogen at -196°C.

The acid strength of the catalysts was measured qualitatively by usual method after the pretreatment using a series of Hammett indicators. The catalysts were pretreated in glass tubes by the same procedure as for the reactions. They were cooled to room temperature and filled with dry nitrogen. The color change of series of indicators were observed for each catalyst by the spot test under dry nitrogen atmosphere. Infrared spectra of various catalyst were recorded to examine the thermal stability of adsorbed sulfate ions on the catalyst, using JASCO IR-2 spectrometer. For the i.r. measurements of CO adsorption, the sample was pressed into wafers weighing about 8 mg/cm^2. The wafer was placed in a heatable vacuum cell and evacuated at 400°C for 1.5 hr. After cooling to room temperature, the i.r. spectrum of the pretreated sample was recorded. The sample was then exposed to CO of 190 torr for 30 min and the i.r. spectrum was taken. Then the cell was re-evacuated for 30 sec and the i.r. spectrum was taken. X-ray diffractograms were taken by JEOL model JDX-88 X-ray diffractometer with copper target and nickel filter at 30KV and 1000 cps. The thermal analysis was carried out with Rigaku Denki Thermoflex in air. The sulfur content was determined according to the Korean industrial standard method (KS D 1830).

RESULTS AND DISCUSSION

X-ray diffraction pattern

The physical or chemical structure of a catalyst varies with the method of preparation and the condition of pretreatment, and consequently affects the catalytic activities profoundly. The precipitation from a mixed solution of the various mole ratio of $NiCl_2$ to $ZrOCl_2$ with ammonium hydroxide was terminated at pH 8. This series of catalysts are denoted by following a mole percent of nickel oxide. For example, 25-catalyst means the catalyst having 25 mole percentage of the nickel oxide.

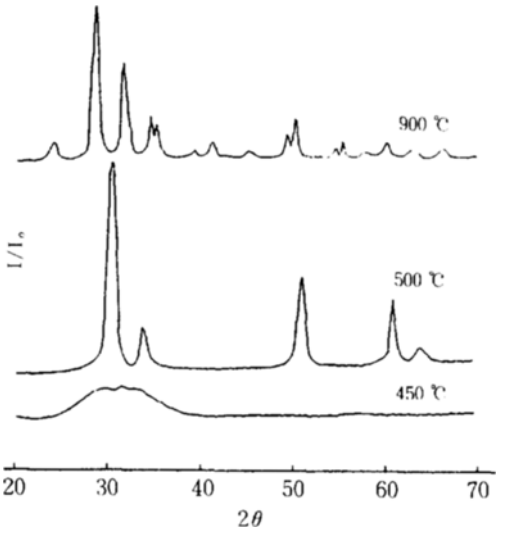

Fig. 1. X-ray diffraction patterns of 25-catalyst decomposed at various temperature.

Fig. 1 presents X-ray diffraction patterns of coprecipitate and 25-catalyst treated with 1N H_2SO_4. The coprecipitate of $Ni(OH)_2$-$Zr(OH)_4$ was found to be amorphous. However, the structure of sample decomposed in air varied depending on the calcination temperature as shown in Fig. 1. 25-catalyst showed amorphous structure up to 400°C and very poor crystalline at 450°C. On the other hand, the tetragonal phase of ZrO_2 was observed at 500°C, whereas monoclinic phase at 900°C. Three crystal structures of ZrO_2, tetragonal, monoclinic and cubic phases have been reported [16,17]. For 60-catalyst having high content of nickel, the cubic phase of NiO was observed at 500°C. However, for any catalysts, the formation of nickel sulfate or zirconium sulfate due to the H_2SO_4 treatment was not observed. As will be discussed in the following section, the structural change of catalyst affects the catalytic activity and specific surface area.

Thermal analysis

In X-ray diffraction patterns, it was shown that the structure of catalyst was different depending on the calcined temperature. To examine the thermal properties of coprecipitate more clearly, its thermal analysis was carried out and illustrated in Fig. 2. For 25-catalyst, two maxima of endothermic peak appeared at 110°C and 300°C, respectively. It seems that the first peak in the range of 30-180°C is attributed to the removal of adsorbed and hydrated water, while the second peak in the range of 230-330°C is responsible for the decomposition of coprecipitate. The decomposition of nickel hydroxide is known to begin at 230°C [18]. The exothermic peak in the range of 455-520°C is attributed to

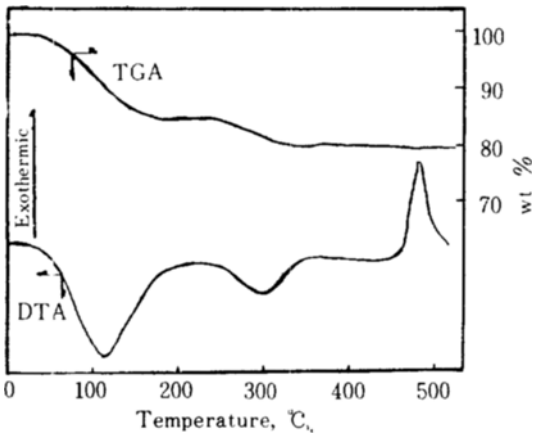

Fig. 2. DTA and TGA curves of coprecipitate of $Ni(OH)_2$-$Zr(OH)_4$.

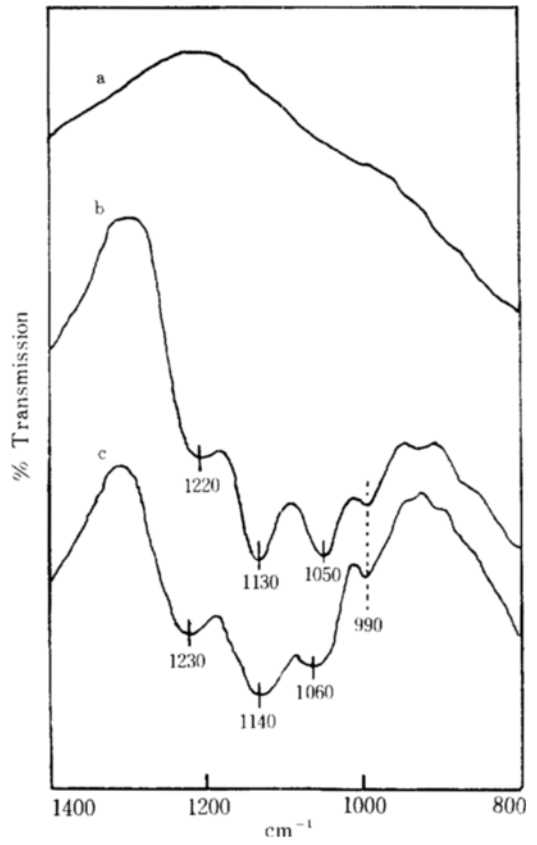

Fig. 3. Infrared spectra of 25-catalyst treated with H_2SO_4: (a) $Ni(OH)_2$-$Zr(OH)_4$, (b) $Ni(OH)_2$-$Zr(OH)_4$ treated with 1N H_2SO_4, (c) $Ni(OH)_2$-$Zr(OH)_4$ treated with 1N H_2SO_4 followed by evacuating at 400℃ for 1.5 hr.

the transition from amorphouse to tetragonal phase. This result is in agreement with that of X-ray diffraction. Namely, tetragonal structure was observed by calcining the catalyst at 500°C for 1.5hr.

Infrared spectra

The infrared spectra of 25-catalyst treated with 1N H_2SO_4 are given in Fig. 3. The catalyst showed infrared absorption bands at 1220-1230, 1130-1140, 1050-1060, 990 cm^{-1} which are assigned to the bidendate sulfate ion coordinated to the metal [19]. The ν SO spectra from the adsorbed sulfate in the ν_1 and ν_3 frequency region (900-1400cm^{-1}) support a species of reduced C_2 ν symmetry with four bands arising from ν_1 and splitting of the triply degenerate ν_3 vibration [20]. Other catalysts treated with sulfate ion of different concentrations also showed similar infrared absorption bands. Even after evacuation at 400°C for 1.5hr, strong absorption bands of sulfate ion remained to indicate a very strong interaction between sulfate ion and Zr^{+4}or Ni^{+2} As will be discussed in the following section, the sulfate ion coordinated to the metal enhances the acid strength of the catalyst and consequently is responsible for the catalytic activity of olefin dimerization.

Dimerization of olefins

The relative reactivity of ethylene, propylene and 1-butene was measured at 20°C by static system using 25-catalyst evacuated at 400°C for 1.5 hr. The pressure change with reaction time is illustrated in Fig.

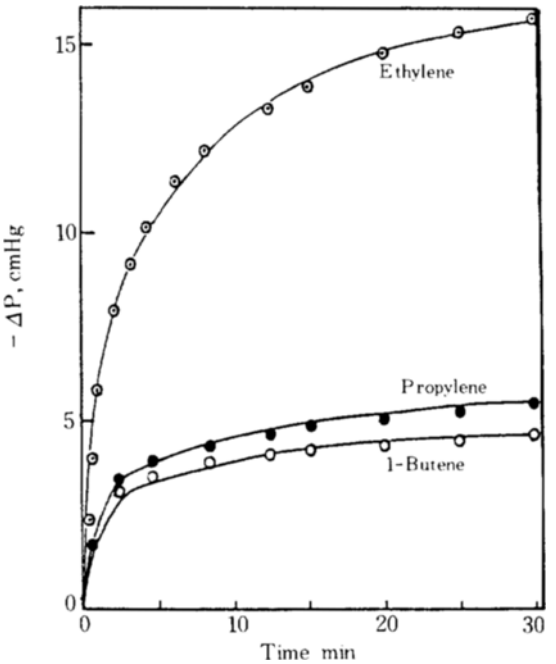

Fig. 4. Pressure change of olefins during the course of dimerization over 25-catalyst.

4. Ethylene was continuously consumed, while the pressure change of propylene and 1-butene was slow as compared with that of ethylene. In this paper, emphasis has been placed to the dimerization reaction of ethylene.

Effect of SO_4^{-2} content

The catalytic activity of 25-catalyst treated with H_2SO_4 of different concentrations was examined, and the results are given in Fig. 5. The maximum activity was observed at about 4% of SO_3 content or 1N concentration of H_2SO_4. Hereafter, if there is no special mention, catalyst means the sample treated with 1N H_2SO_4 followed by decomposing it at 200°-600°C. The samples which were not treated with H_2SO_4 were inactive as catalyst for ethylene dimerization. It is probably considered that the activity decrease above 4% of SO_3 content is explained in terms of the decrease of the number of active sites due to the adsorption of large amount of sulfate ion.

Initial product of ethylene dimerization

Over 25-catalyst, ethylene was selectively dimerized to n-butenes. In the composition of n-butenes analyzed by gas chromatography, 1-butene was found to predominate exclusively at the initial reaction time as compared with 2-butene. As shown in Fig. 6, however, the amount of 1-butene decreases with the reaction time, while the amount of 2-butene increases with time. Therefore, it is very clear that the initial product of ethylene dimerization is 1-butene and the produced 1-butene is also isomerized to 2-butene during the reaction time. It was found that the activity decrease is accompanied by a decrease in the extent of isomerization of n-butene produced by the dimerization. The compositions of n-butene obtained by dimerization runs on a series of catalysts for 30 min are plotted against the catalyst composition of NiO-ZrO_2/SO_4^{-2} system in Fig. 7. It is obvious that the selectivity to 2-butene runs parallel with its dimerization activity.

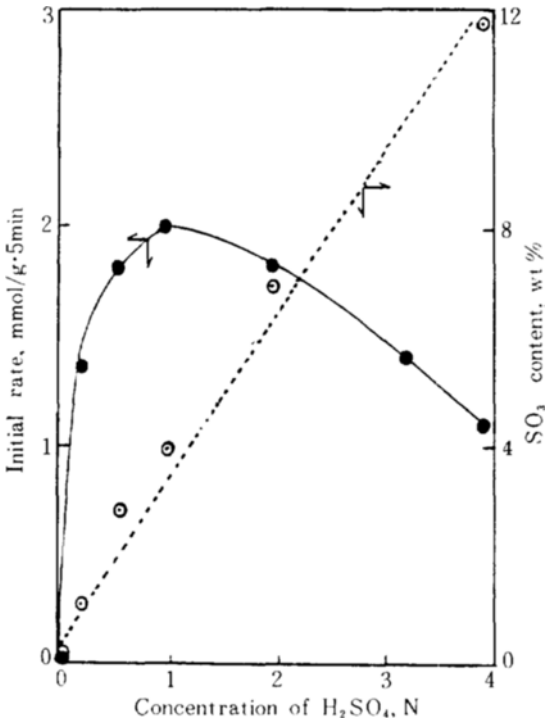

Fig. 5. Relationship between initial rate for ethylene dimerization and SO_3 content of 25-catalyst treated with different concentration of H_2SO_4.

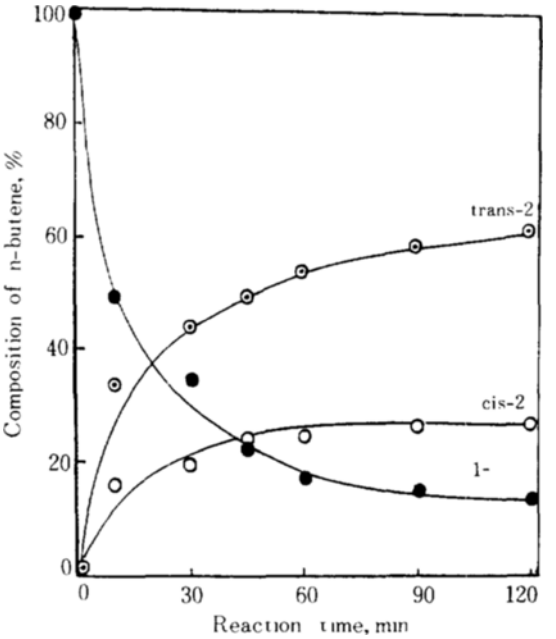

Fig. 6. Composition change of produced n-butenes with reaction time. Reaction conditions: 25-catalyst(0.2g) evacuated at 400℃ for 1.5hr; reaction temperature = 20℃, ethylene initial pressure = 185 torr.

Effect of catalyst composition

The effect of catalyst composition on the initial rate was examined, where the catalysts were evacuated at 400°C for 1.5 hr. As shown in Fig. 7, the maximun activity is obtained with the catalyst of 25 mole percent of nickel oxide. This means to be due to the increase of specific surface area and the subsequent increase of active site. In fact Fig. 7 shows that the specific surface area attained a maximum when the content of NiO in catalyst is 25 mole percent.

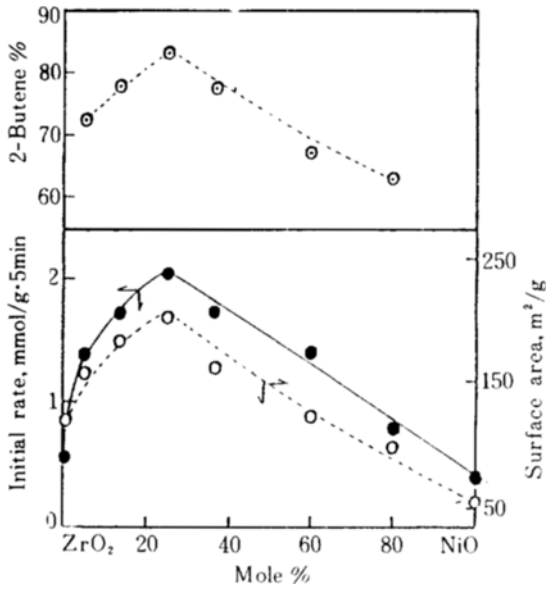

Fig. 7. Variation of initial rate, product composition in ethylene dimerization, and specific surface area with the catalyst composition of NiO-ZrO_2/SO_4^{-2}system.

Effect of evacuation temperature

In Fig. 8, the ethylene dimerization activities of 25-catalysts are plotted against evacuation temperature at which the catalyst was evacuated for 1.5 hr. It can be seen that the activity appears above 200°C reaching a maximum at 400-450°C. In Fig. 2, the decomposition of coprecipitate was observed to begin at 230°C. The decomposition of nickel hydroxide is known to begin at 230°C [18]. Therefore, it is very likely that the activation of catalyst above 200°C is related to the decomposition of the catalyst.

Fig. 8 also shows the gradual decrease of activity after the evacuation temperature above 450°C. It would be worthwhile to discuss the activity decrease above 450°C. As shown in Fig. 1, the catalyst showed nearly amorphous structure up to 450°C, while above 450°C the catalyst structure was changed from amorphous phase to tetragonal phase. The activity decrease above 450°C is reasonably explained by the solid phase rearrangement or sintering of the catalyst as demonstrated by irreversible decrease of specific surface area (Fig. 8). The effect of calcination temperature on the acidic properties of pure alumina was reported [21]. η-Al_2O_3 calcined at 500°C had low crystallinity and maximum activity, while that calcined at 600°C exhibited high crystallinity and minimum activity. Therefore, it is very important that the catalyst of high catalytic activity and surface area should be amorphous.

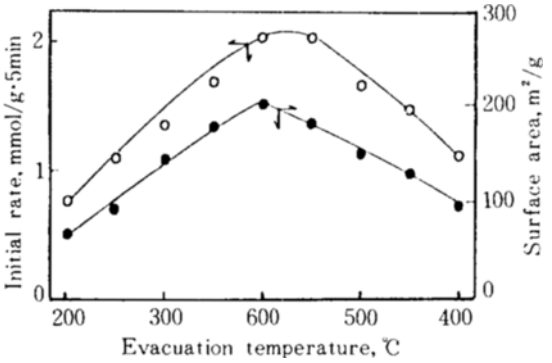

Fig. 8. Variation of initial rate for ethylene dimerization and specific surface area with evacuation temperature.

Active sites

It is remarkable that the samples which were not treated with H_2SO_4 were inactive as catalyst for ethylene dimerization, but the sample treated with H_2SO_4 exhibited high catalytic activity. The active site responsible for dimerization is suggested to consist of a low valent nickel ion and an acid as observed in the NiO-SiO_2 catalyst [4, 22]. The term "low valent nickel" originated from the fact that the NiO-SiO_2 catalyst was drastically poisoned by carbon monoxide, since a low valent nickel is favorable to chemisorb carbon monoxide [22]. In the

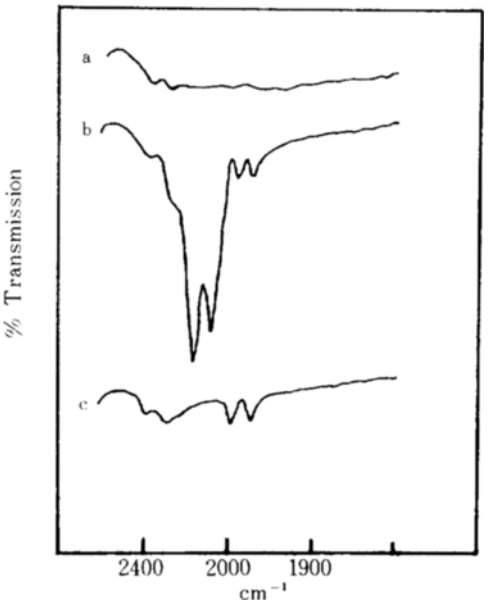

Fig. 9. Infrared spectra of CO adsorbed on 25 catalyst. (a) Back ground of 25-catalyst evacuated at 400℃ for 1.5hr, (b) Exposed to CO of 190 torr for 30min, (c) Evacuated at room temperature for 30sec.

system of $NiO\text{-}ZrO_2/SO_4^{-2}$ the catalyst was poisoned by 1 μmol/g of carbon monoxide for dimerization. Fig. 9 shows the infrared spectra of CO adsorbed on catalyst. After exposing 25-catalyst to CO for 30 min followed by the evacuation, the absorption bands were observed at 1995 and 1973 cm^{-1}. These bands were lower in wave number than those at 2217 cm^{-1} attributed to the interaction between CO and Ni^{2+} and those at 2188 cm^{-1} attributed to the interaction between CO and Ni^{1+} [23]. Therefore, these absorption bands could be attributed to the CO adsorbed on metallic nickel which was formed by the evacuation at high temperatures.

The nickel oxide treated with H_2SO_4 exhibited a little activity for dimerization as shown in Fig. 7, but nickel oxide without sulfate ion was inactive. These results support more confirmly the fact that the active site for dimerization is formed by an interaction of a low valent nickel ion with an acid. In fact ZrO_2/SO_4^{-2} alone without nickel ion was inactive for dimerization although it exhibited a little activity for polymerization. It is well known that acid catalyst is effective for the polymerization of olefins [21].

Acid properties

It has been established that protonic and nonprotonic acid sites are distinguishable by infrared spectra of adsorbed pyridine [24]. In the infrared spectra of pyridine adsorbed on 25-catalyst, both the pyridinium ion band at 1540 cm^{-1} and the coordinated pyridine band at 1450 cm^{-1} was found to indicate the presence of both Lewis and Brönsted acids. As mentioned above, the samples without sulfate ion were not effective for ethylene dimerization. This means that the samples do not have enough acid strength to catalyze the dimerization reaction. Zirconium oxide prepared by calcining zirconium hydroxide at 300-700°C has weak acid strength of $4.8 < Ho \leq 6.8$ [25]. The acid strength of the present samples treated with H_2SO_4 was examined by a color change method using Hammett indicators. Since it was very difficult to observe the color of indicators adsorbed on the catalyst of high content of nickel oxide, a low percent of nickel oxide (5-catalyst) was used in this experiment. The results are listed in Table 1. In this table + means that the color of base form was changed to that of conjugate acid form. Since the color of all used indicators was changed, the acid strength of the present catalyst is at least to be $Ho \leq -14.5$. However, the acid strength of the sample without sulfate ion was found to be $Ho \leq -3.0$. This is why the sample which was not treated with H_2SO_4 was inactive as catalyst for ethylene dimerization.

Table 1. Measurement of the acid strength of 5-catalyst.

Hammett Indicator	pKa value of Indicator	Evacuation Temperature (400 °C)	
		5-Catalyst with SO_4^{-2}	5-Catalyst without SO_4^{-2}
Dicinnamalacetone	−3.0	+	+
Benzalacetophenone	−5.6	+	−
Anthraquinone	−8.2	+	−
Nitrobenzene	−12.4	+	−
2,4-Dinitrofluorobenzene	−14.5	+	−

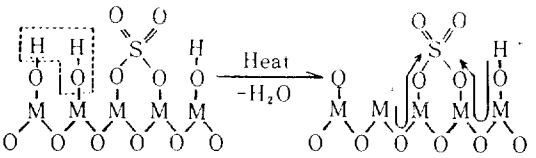

Fig. 10. A model of acid sites generated by the interaction with sulfate ion.

The acid stronger than $Ho \leq -11.93$, which correspond to the acid strength of 100% H_2SO_4, is known as superacid [26]. Consequently, the present catalyst would be a solid superacid. Superacidic properties are attributed to the double bond nature of S = O of the complex formed by the interaction of $NiO\text{-}ZrO_2$ with sulfate ion. Both Lewis and Brönsted acid strength becomes stronger by the inductive effect of S = O in the complex as illustrated in Fig. 10. Enhancement of electron deffiency on M^+ and OH bond by the interaction of sulfate ion is the origin of superacidic properties.

CONCLUSION

A series of catalyst $NiO\text{-}ZrO_2/SO_4^{-2}$ was found to be very active for ethylene dimerization and the following fact is demonstrated in the present study.

1. $NiO\text{-}ZrO_2/SO_4^{-2}$ is very effective for ethylene dimerization, but $NiO\text{-}ZrO_2$ alone without SO_4^{-2} does not exhibit catalytic activity absolutely.
2. The high catalytic activity of $NiO\text{-}ZrO_2/SO_4^{-2}$ is closely correlated with the increase of acid strength by the inductive effect of sulfate ion coordinated to Zr^{+4} or Ni^{2+}.
3. The active site for dimerization is formed by an interaction of a low valent nickel ion with an acid, because the sample without either nickel ion or sulfate ion was inactive for dimerization.
4. The decrease of catalytic activity above 450°C can be explained in terms of the transition of catalyst from amorphouse phase to crystalline and the sintering of catalyst.

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