

Effect of Al₂O₃ Addition and WO₃ Modification on Catalytic Activity of NiO/Al₂O₃-TiO₂/WO₃ for Ethylene Dimerization

Young Il Pae[†] and Jong Rack Sohn^{*}

Department of Applied Chemistry, Engineering College, Kyungpook National University, Daegu 702-701, Korea

^{*}E-mail: jrsohn@knu.ac.kr

[†]Department of Chemistry, University of Ulsan, Ulsan 680-746, Korea

Received July 24, 2007

Strong solid acid catalysts, NiO/Al₂O₃-TiO₂/WO₃ for ethylene dimerization were prepared by the addition of Al₂O₃ and the modification with WO₃. The acid sites and acid strength were increased by the inductive effect of WO₃ species bonded to the surface of catalysts. The larger the dispersed WO₃ amount, the higher both the acidity and catalytic activity for ethylene dimerization. The addition of Al₂O₃ to TiO₂ up to 5 mol% enhanced acidity and catalytic activity gradually due to the interaction between Al₂O₃ and TiO₂ and consequent formation of Al-O-Ti bond.

Key Words : Al₂O₃ addition, WO₃ modification, Acidity, Ethylene dimerization

Introduction

Heterogeneous catalysts for the dimerization and oligomerization of olefins, consisting mainly of nickel compounds supported on oxides, have been known for many years. A considerable number of papers have dealt with the problem of nickel-containing catalysts for ethylene dimerization.¹⁻¹¹ One of the remarkable features of this catalyst system is its activity in relation to a series of *n*-olefins. In contrast to usual acid-type catalysts, nickel oxide on silica or silica-alumina shows a higher activity for a lower olefin dimerization, particularly for ethylene.^{1-6,12} It has been suggested that the active site for dimerization is formed by an interaction of a low-valent nickel ion with an acid site.^{9,13} In fact, nickel oxide, which is active for C₂H₄-C₂D₄ equilibration, acquires an activity for ethylene dimerization upon addition of nickel sulfate, which is known to be an acid.¹⁴ A transition metal can also be supported on zeolite in the state of a cation or a finely dispersed metal. Transition metal ions like Ni⁺ or Pd⁺ can be active sites in catalytic reactions such as ethylene and propylene dimerization as well as acetylene cyclomerization.¹⁵⁻¹⁷

The previous papers from this laboratory have shown that NiO-TiO₂ and NiO-ZrO₂ modified with sulfate or tungstate ions are very active for ethylene dimerization.^{6,18-20} High catalytic activities in the reactions were attributed to the enhanced acidic properties of the modified catalysts, which originated from the inductive effect of S=O or W=O bonds of the complex formed by the interaction of oxides with sulfate or tungstate ions. However, catalytic functions have been improved by loading additional components. Sulfated zirconia incorporating Fe and Mn has been shown to be highly active for butane isomerization, catalyzing the reaction even at room temperature.^{21,22} The promotion in activity of catalyst has been confirmed by several other research group.²³⁻²⁵ Coelho et al. have discovered that the addition of Ni to sulfated zirconia causes an activity enhancement com-

parable to that caused by the addition of Fe and Mn.²⁶ It has been reported by several workers that the addition of platinum to zirconia modified by sulfate ions enhances catalytic activity in the skeletal isomerization of alkanes without deactivation when the reaction is carried out in the presence of hydrogen.²⁷⁻²⁹ Recently, it has been found that a main group element Al can also promote the catalytic activity and stability of sulfated zirconia for *n*-butane isomerization and ethylene dimerization.³⁰⁻³²

The search for a more active catalyst is a never ending task. At the same time that increased catalytic activity is sought, an improvement in selectivity to the desired product is also required. Recently, some workers reported zirconia or titania-supported WO₃ as alternative materials in reactions requiring strong acid sites.³³⁻³⁶ Several advantages of tungstate over sulfate as dopant include the facts that they do not suffer from dopant loss during thermal treatment and that they undergo significantly less deactivation during catalytic reaction.³⁶ It is known that for titania-supported catalyst its surface area and catalytic activity are decreasing under the severe reaction condition. To overcome these deficiencies, titania was added by Al₂O₃ and was modified with WO₃ by taking advantage of high acidity, high thermal stability, and high surface area of modified TiO₂. In this paper we report new catalyst systems prepared by adding Al₂O₃ to TiO₂ and modifying TiO₂ with WO₃ for ethylene dimerization.

Experimental

Catalyst preparation. The Al₂O₃-TiO₂ mixed oxide was prepared by a co-precipitation method using aqueous ammonia as the precipitation reagent. The coprecipitate of Al(OH)₃-Ti(OH)₄ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of titanium tetrachloride and aluminum nitrate (Junsei Chemical Co.) at room temperature with stirring until the pH of the mother liquor reached about 8. NiO/Al₂O₃-TiO₂ was prepared by

adding aqueous ammonia slowly into a mixed solution of NiCl_2 solution and $\text{Al}(\text{OH})_3\text{-Ti}(\text{OH})_4$ with stirring until the pH of solution reached about 8. The catalysts containing various tungsten oxide contents were prepared by adding an aqueous solution of ammonium metatungstate [$(\text{NH}_4)_6\text{-(H}_2\text{W}_{12}\text{O}_{40})\cdot n\text{H}_2\text{O}$] to the $\text{NiO}/\text{Al}_2\text{O}_3\text{-TiO}_2$ powder followed by drying and calcining at high temperatures for 1.5 h in air. This series of catalysts are denoted by their weight percentage of NiO and WO_3 . For example, 20NiO/5Al₂O₃-TiO₂/15WO₃ indicates the catalyst containing 20 wt% NiO, and 15 wt% WO_3 , and 5 mol% Al₂O₃ regarding only TiO₂.

Procedure. FTIR spectra were obtained in a heatable gas cell at room temperature using a Mattson Model GL6030E spectrophotometer. The self-supporting catalyst wafers contained about 9 mg cm⁻². Prior to obtaining the spectra, we heated each sample under vacuum at 100-400 °C for 1 h. Catalysts were checked in order to determine the structure of the prepared catalysts by means of a Philips X'pert-APD X-ray diffractometer, employing Ni-filtered Cu K_α radiation.

The specific surface area was determined by applying the BET method to the adsorption of N₂ at -196 °C. Chemisorption of ammonia was also employed as a measure of the acidity of catalysts. The amount of chemisorption was determined based on the irreversible adsorption of ammonia.³⁷⁻³⁹

The catalytic activity for ethylene dimerization was determined at 20 using a conventional static system following the pressure change from an initial pressure of 290 Torr. A fresh catalyst sample of 0.2 g was used for every run and the catalytic activity was calculated as the amount of ethylene consumed during initial 5 min. Reaction products were analyzed by gas chromatography with a VZ-7 column at room temperature.

Results and Discussion

Infrared spectra of WO_3 species. To examine the structure of tungsten oxide complex under dehydration conditions, infrared spectra of 20NiO/5Al₂O₃-TiO₂/15WO₃ samples were obtained in a heatable gas cell after evacuation at different temperatures for 1 h. The in situ infrared spectra in the 900-1100 cm⁻¹ region for 20NiO/5Al₂O₃-TiO₂/15WO₃ are presented in Figure 1. The infrared single band at 1003-1012 cm⁻¹ is due to the symmetrical W=O stretching mode of the tungsten oxide complex coordinated to the Al₂O₃-TiO₂ surface.⁴⁰ As shown in Figure 1, as evacuation temperature increases, the W=O stretching mode shifts upward from 1003 to 1012 cm⁻¹, the band becomes sharper, and the intensity increases. The similar results have been obtained with the other samples. This shows that the dehydration changes the molecular structures and that the two-dimensional tetrahedrally coordinated tungsten oxide species as well as the octahedrally coordinated polytungstate species are converted into the same highly distorted octahedrally coordinated structure as proposed for the WO_3/TiO_2 system by Wachs *et al.*⁴¹ For the other 20NiO/5Al₂O₃-TiO₂/WO₃ samples containing different WO_3 contents and evacuated at 400 °C the band intensity at 1012 cm⁻¹ increased with

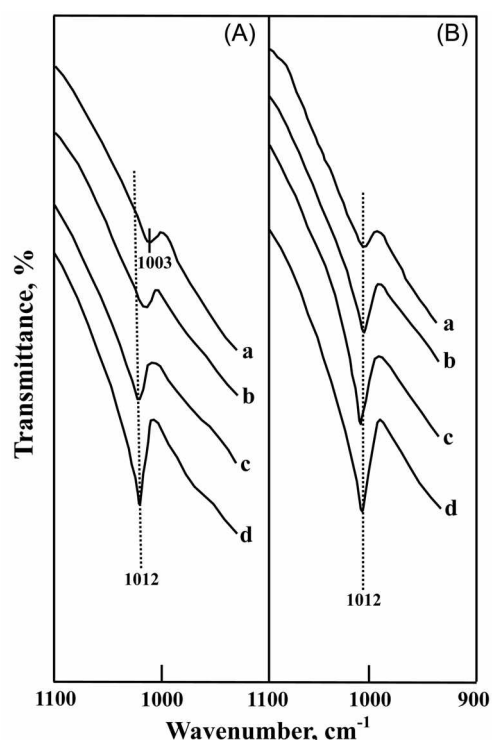


Figure 1. (A) Infrared spectra of 20NiO/5Al₂O₃-TiO₂/15WO₃ evacuated at different temperatures for 1 h: (a) 100 °C (b) 200 °C (c) 300 °C and (d) 400 °C. (B) Infrared spectra of 20NiO/5Al₂O₃-TiO₂/WO₃ containing different WO_3 contents and evacuated at 400 °C for 1 h: (a) 20NiO/5Al₂O₃-TiO₂/3WO₃ (b) 20NiO/5Al₂O₃-TiO₂/5WO₃ (c) 20NiO/5Al₂O₃-TiO₂/10WO₃ and (d) 20NiO/5Al₂O₃-TiO₂/15WO₃.

increasing the WO_3 content, indicating that the higher the WO_3 content, the more the octahedrally coordinated WO_3 species.

Crystalline structures of catalysts. The crystalline structures of catalysts calcined in air at different temperatures for 1.5 h were examined. In the case of titania support, as shown in Figure 2, TiO₂ was amorphous to X-ray diffraction at 25 °C, with an anatase phase 300-400 °C, a two-phase mixture of the anatase and rutile forms at 500-600 °C, and a rutile phase at 700-800 °C. Three crystal structures of TiO₂, *i.e.*, anatase, rutile, and brookite phases have been reported.^{42,43} However, in the case of 5Al₂O₃-TiO₂, the crystalline structures of the samples were different from that of pure TiO₂. As shown in Figure 3, 5Al₂O₃-TiO₂ calcined at 400 °C are mostly amorphous. The transition temperature of TiO₂ from amorphous to anatase phase was higher by 200 °C than that of pure TiO₂. X-ray diffraction data indicated only the anatase phase of TiO₂ at 500-800 °C, showing that the amount of anatase TiO₂ phase increased with increasing the calcination temperature. It is assumed that the interaction between Al₂O₃ and TiO₂ hinders the phase transition of TiO₂ from amorphous to anatase.^{32,44,45}

The XRD patterns of 20NiO/5Al₂O₃-TiO₂/WO₃ calcined at 400 °C for 1.5 h as a function of WO_3 content are shown in Figure 4. WO_3 remained amorphous to X-ray diffraction up to 15 wt%, indicating good dispersion on the surface of

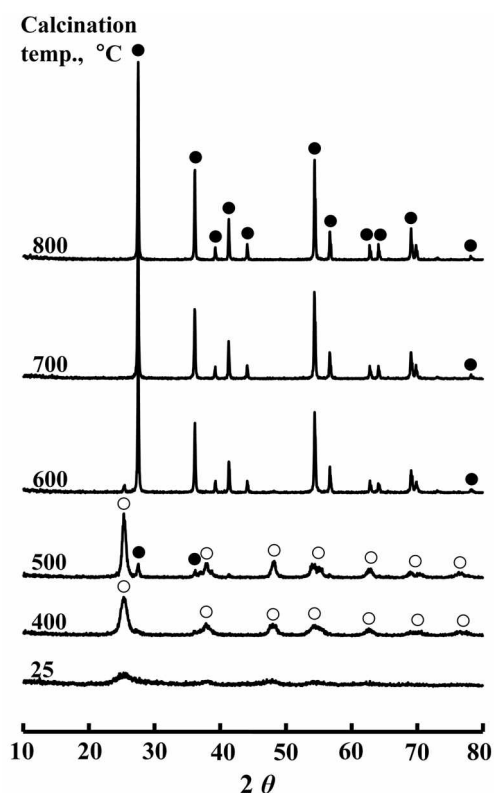


Figure 2. X-ray diffraction patterns of TiO₂ calcined at different temperatures for 1.5 h: (○), anatase phase of TiO₂; (●), rutile phase of TiO₂.

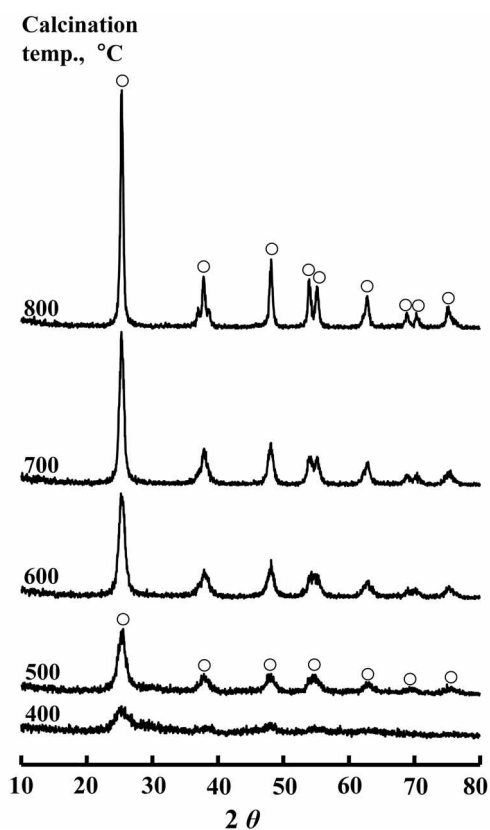


Figure 3. X-ray diffraction patterns of 5Al₂O₃-TiO₂ calcined at different temperatures for 1.5 h: (○), anatase phase of TiO₂.

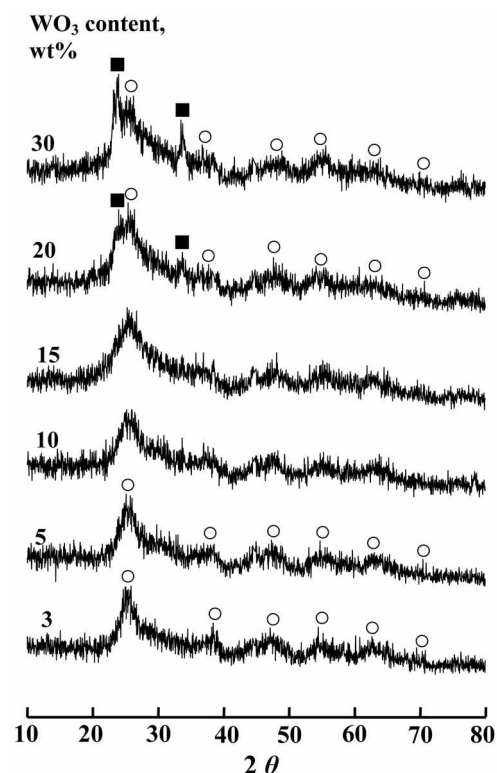


Figure 4. X-ray diffraction patterns of 20NiO/5Al₂O₃-TiO₂/WO₃ containing different WO₃ contents and calcined at 400 °C for 1.5 h: (○), anatase phase of TiO₂; (■), monoclinic phase of WO₃.

catalyst. However, from 20 wt% of WO₃, the XRD data indicated the presence of a two-phase mixture of monoclinic phase of WO₃ and anatase phase of TiO₂, where the crystallinity of anatase phase TiO₂ was very poor due to the interaction between TiO₂ and the other oxides. In general, for the calcination temperature of 400-500 °C the hexagonal and monoclinic phases of WO₃ are present.⁴⁶ However, in case of 20NiO/Al₂O₃-TiO₂/WO₃ containing WO₃ content above 15 wt%, only the monoclinic phase of WO₃ was observed, as shown in Figure 4.

NiO was amorphous to X-ray diffraction regardless of NiO content up to 30 wt% of NiO, indicating excellent dispersion on the surface of catalyst. For the above Al₂O₃-promoted catalysts, there are no characteristic peaks of Al₂O₃ in the XRD patterns, implying that Al₂O₃ is sufficiently homogeneously mixed with titania.

The crystalline structures of 20NiO/5Al₂O₃-TiO₂/15WO₃ calcined in air at different temperatures for 1.5 h were examined. As shown in Figure 5, the catalyst was amorphous to X-ray diffraction up to 400 °C. However, for the calcination temperature of 500 °C XRD data indicated a two-phase mixture of monoclinic phase of WO₃ and anatase phase of TiO₂. The amount of two phases of TiO₂ and WO₃ increased with increasing calcination temperature, indicating that the interaction between NiO or WO₃ and TiO₂ hinders the transition of TiO₂ from amorphous to anatase phase.^{44,47} The presence of NiO and WO₃ strongly influences the development of textural properties with temperature in

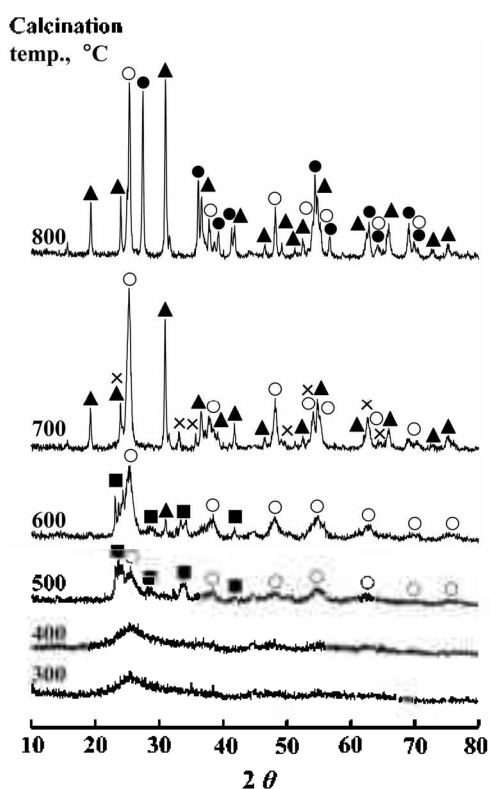


Figure 5. X-ray diffraction patterns of 20NiO/5Al₂O₃-TiO₂/15WO₃ calcined at different temperatures for 1.5 h: (○), anatase phase of TiO₂; (●), rutile phase of TiO₂; (■), monoclinic phase of WO₃; (▲), monoclinic phase of NiWO₄; (×), rhombohedral phase of NiTiO₃.

comparison with pure TiO₂. In fact, it is reported that for pure TiO₂ two phases of anatase and rutile TiO₂ are present at the calcination temperature of 350 °C because of no interaction of titania.⁴⁷ No phase of NiO was observed in any phase at all calcination temperature, indicating good dispersion of NiO on the surface of TiO₂ support due to the interaction between them. For the calcination temperature of 600 °C a new phase of monoclinic nickel tungstate (NiWO₄) was observed through the reaction between NiO and WO₃, showing that the amount of nickel tungstate increased with increasing calcination temperature, as shown in Figure 5. For the calcination temperature of 700 °C a phase of rhombohedral nickel titanate (NiTiO₃) was observed newly through the reaction between NiO and TiO₂, but this phase disappeared at the calcination temperature of 800 °C due to the decomposition of NiTiO₃. For the calcination temperature of 800 °C a phase transition from anatase TiO₂ to rutile TiO₂ occurred, showing the presence of a three-phase mixture of the anatase and rutile forms, and nickel tungstate.

Surface properties. The specific surface areas of 20NiO/5Al₂O₃-TiO₂/WO₃ catalysts containing different WO₃ contents and calcined at 400 °C for 1.5 h are listed in Table 1. The presence of WO₃ also influences the surface area. The surface area increases gradually with increasing tungsten oxide loading up to 15 wt%. It seems likely that the interactions between tungsten oxide (or Al₂O₃) and TiO₂ prevent

Table 1. Specific surface area and acidity of 20-NiO/5Al₂O₃-TiO₂/WO₃ catalysts containing various WO₃ contents and calcined at 400 °C for 1.5 h

| WO ₃ content, wt% | Surface area, m ² /g | Acidity, μmol/g |
|------------------------------|---------------------------------|-----------------|
| 0 | 200 | 192 |
| 3 | 257 | 210 |
| 5 | 262 | 213 |
| 10 | 269 | 221 |
| 15 | 285 | 247 |
| 20 | 236 | 226 |
| 30 | 226 | 220 |

catalysts from crystallizing.³³ The decrease of surface area for 20NiO/5Al₂O₃-TiO₂/WO₃ samples containing WO₃ above 15 wt % is also due to the blocking of TiO₂ pores by the increased WO₃ loading. The acidity of catalysts calcined at 400 °C, as determined by the amount of NH₃ irreversibly adsorbed at 230 °C,^{37-39,44,48} is also listed in Table 1. It seems likely that strong acid sites are formed through the bonding between dispersed WO₃ and TiO₂. Similarly to the case of sulfated metal oxides, the new acid sites can be formed and the acid strength can be strongly enhanced by the inductive effect of tungstate ion bonded to the surface of catalyst.^{33,49}

We examined the effect of Al₂O₃ addition on the surface area and acidity of 20NiO/Al₂O₃-TiO₂/15WO₃ samples. The specific surface areas and acidity of 20NiO/Al₂O₃-TiO₂/15WO₃ catalysts containing different Al₂O₃ contents and calcined at 400 °C are listed in Table 2. Both surface area and acidity increased with increasing Al₂O₃ content up to 5 mol%, indicating the promoting effect of Al₂O₃ on the catalytic activity for ethylene dimerization described later.

The specific surface areas of NiO/5Al₂O₃-TiO₂/15WO₃ catalysts containing different NiO contents and calcined at 400 °C for 1.5 h were examined. The presence of NiO influences the surface area in comparison with that of the pure TiO₂. Specific surface areas of 5NiO/5Al₂O₃-TiO₂/15WO₃ (260 m²g⁻¹) and 20NiO/5Al₂O₃-TiO₂/15WO₃ (285 m²g⁻¹) samples are larger than that of 5Al₂O₃-TiO₂ (93 m²g⁻¹) calcined at the same temperature, showing that surface area increases gradually with increasing nickel oxide loading up to 20 wt%. It seems likely that the interactions between nickel oxide and TiO₂ prevent catalysts from crystallizing.³³ The decrease of surface area for NiO/5Al₂O₃-TiO₂/15WO₃ samples containing NiO above 20 wt % is also

Table 2. Specific surface area and acidity of 20-NiO/Al₂O₃-TiO₂/15WO₃ catalysts containing various Al₂O₃ contents and calcined at 400 °C for 1.5 h

| Al ₂ O ₃ content, mol % | Surface area, m ² /g | Acidity, μmol/g |
|---|---------------------------------|-----------------|
| 0 | 172 | 182 |
| 1 | 193 | 193 |
| 2 | 240 | 230 |
| 3 | 250 | 241 |
| 5 | 285 | 247 |
| 7 | 269 | 184 |
| 10 | 234 | 161 |

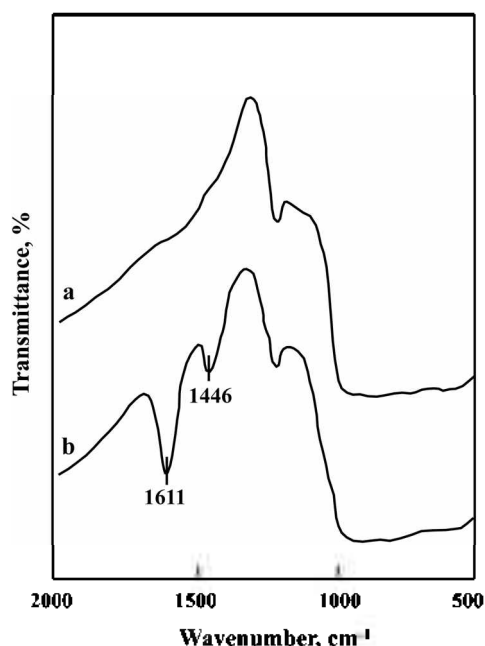


Figure 6. Infrared spectra of NH₃ adsorbed on 20NiO/5Al₂O₃-TiO₂/15WO₃: (a) background of 20NiO/5Al₂O₃-TiO₂/15WO₃ after evacuation at 400 °C for 1 h, (b) NH₃ adsorbed on (a), where gas was evacuated at 230 °C for 1 h.

due to the blocking of TiO₂ pores by the increased NiO loading.

Infrared spectroscopic studies of ammonia adsorbed on solid surfaces have made it possible to distinguish between Brønsted and Lewis acid sites.⁵⁰⁻⁵² Figure 6 shows the infrared spectra of ammonia adsorbed on 20NiO/5Al₂O₃-TiO₂/15WO₃ catalyst evacuated at 400 °C for 1 h. For 20NiO/5Al₂O₃-TiO₂/15WO₃, the band at 1446 cm⁻¹ is the characteristic peak of ammonium ion, which is formed on the Brønsted acid sites. The absorption peak at 1611 cm⁻¹ is contributed by ammonia coordinately bonded to Lewis acid sites,⁵⁰⁻⁵² indicating the presence of both Brønsted and Lewis acid sites on the surface of 20NiO/5Al₂O₃-TiO₂/15WO₃ catalyst. Other samples having different NiO and WO₃ contents also showed the presence of both Lewis and Brønsted acids.

Catalytic activities for ethylene dimerization

Effect of calcination temperature on catalytic activity.

The catalytic activities of 20NiO/5Al₂O₃-TiO₂/15WO₃ were tested as a function of calcination temperature. The results are shown in Figure 7, where catalysts were evacuated at 400 °C for 1 h. The activities increased with the calcination temperature, reaching a maximum at 400 °C, and then the activities decreased. The decrease of catalytic activity after calcination above 400 °C can be attributed to the fact that the surface area and acidity above 400 °C decrease with the calcination temperature. As shown in Figure 5, for the calcination temperature above 400 °C various crystalline materials such as tungsten oxide, nickel titanate, nickel tungstate, and titania were formed and consequently the decrease of surface area and acidity gives rise to the decrease

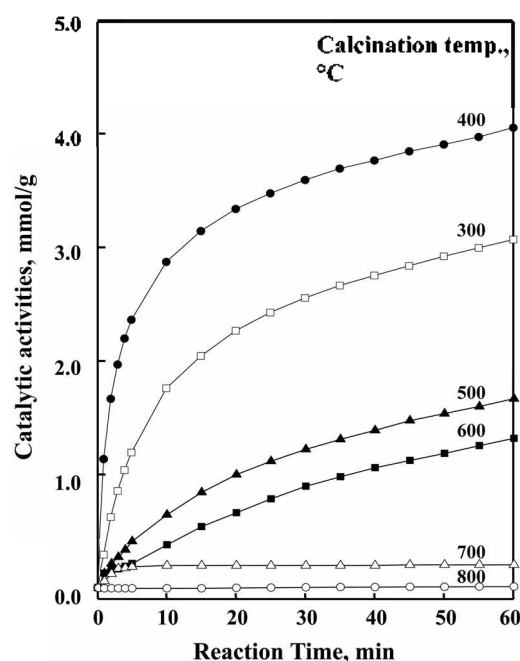


Figure 7. Catalytic activity of 20NiO/5Al₂O₃-TiO₂/15WO₃ at 20 °C as a function of calcination temperature.

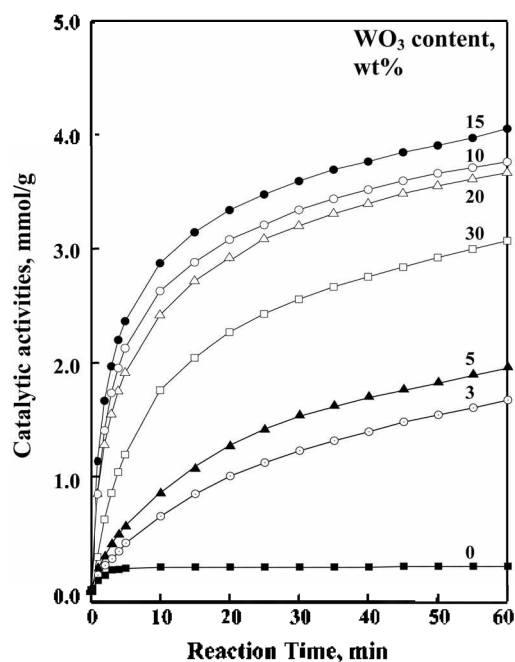


Figure 8. Catalytic activity of 20NiO/5Al₂O₃-TiO₂/WO₃ at 20 °C as a function of WO₃ content.

of catalytic activity. Thus, in our following experiments we placed emphasis on the catalysts calcined at 400 °C.

It was found that over 20NiO/5Al₂O₃-TiO₂/15WO₃, ethylene was continuously consumed, as shown by the results presented in Figure 7. Over all catalysts, ethylene was selectively dimerized to *n*-butenes. However, a small amount of hexenes from the phase adsorbed on the catalyst surface was detected. In the composition of *n*-butenes analyzed by gas chromatography, 1-butene was found to predominate ex-

Table 3. Dispersed WO₃ amount, specific surface area, acidity, and catalytic activity for ethylene dimerization of 20NiO/5Al₂O₃-TiO₂/WO₃ containing different WO₃ contents

| Catalyst | Dispersed WO ₃ amount [WO ₃ (g)/20NiO/5Al ₂ O ₃ -TiO ₂ (g)] | Surface area, m ² /g | Acidity, μmol/g | Catalytic activity, mmol/g |
|--|---|------------------------------------|--------------------|-------------------------------|
| 20NiO/5Al ₂ O ₃ -TiO ₂ /0WO ₃ | 0 | 200 | 192 | 0.2 |
| 20NiO/5Al ₂ O ₃ -TiO ₂ /3WO ₃ | 0.03 | 257 | 210 | 0.4 |
| 20NiO/5Al ₂ O ₃ -TiO ₂ /5WO ₃ | 0.05 | 267 | 213 | 0.7 |
| 20NiO/5Al ₂ O ₃ -TiO ₂ /10WO ₃ | 0.11 | 269 | 221 | 2.1 |
| 20NiO/5Al ₂ O ₃ -TiO ₂ /15WO ₃ | 0.18 | 285 | 247 | 2.3 |

clusively at the initial reaction time, as compared with *cis*-butene and *trans*-butene. This is because the initial product of ethylene dimerization is 1-butene.^{4,9,50} Therefore, the initially produced 1-butene is also isomerized to 2-butene during the reaction time.^{18,19,50,51}

Effect of WO₃ modification on catalytic activity. Recently, it has been reported that metal oxide modified with WO₃ can be used as an alternative catalyst in reactions requiring strong acid sites.³⁴ Several advantages of tungstate over sulfate as dopant include that it does not suffer from dopant loss during thermal treatment and it undergoes significantly less deactivation during catalytic reaction.

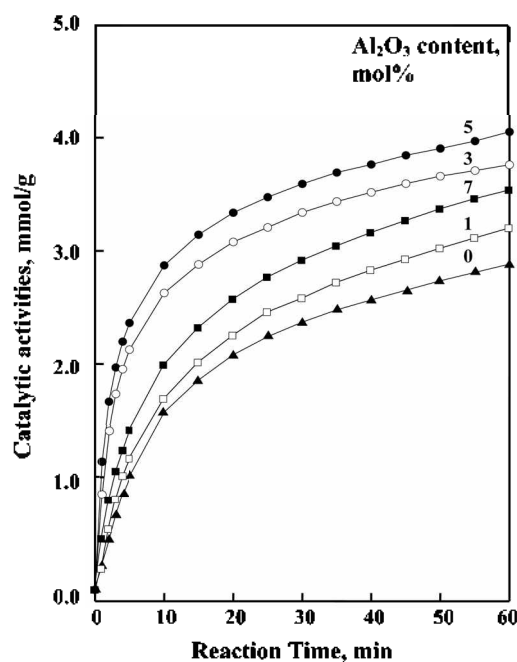
The catalytic activity of 20NiO/5Al₂O₃-TiO₂/WO₃ as a function of WO₃ content is plotted in Figure 8. As shown in Figure 8, the maximum activity is obtained with the catalyst of 15 wt% WO₃, where the amount of dispersed WO₃ is maximum, as listed in Table 3. Therefore, it seems likely that the highest activity of the catalyst containing 15 wt% WO₃ is related to its acidity and acid strength. The high acid strength and acidity are responsible for the W=O bond nature of complex formed by the interaction between WO₃ and TiO₂.^{34,53} As discussed in IR spectra, IR spectra of 20NiO/5Al₂O₃-TiO₂/15WO₃ catalyst after evacuation at 400 °C showed the band at 1012 cm⁻¹ due to the W=O stretching mode of the tungsten oxide complex bonded to the TiO₂ surface.⁵⁴ This isolated tungsten oxide species is stabilized through multiple W-O-Ti bonds between each WO₃ species and the TiO₂ surface.^{55,56} As listed in Table 1, the acidity of 20NiO/5Al₂O₃-TiO₂/15WO₃ catalyst is the most among the catalysts. Of course, the acidity of catalysts is related to their specific surface area, as mentioned above. In fact, Table 1 show that the specific surface area attained a maximum when the WO₃ content in 20NiO/5Al₂O₃-TiO₂/WO₃ catalysts is 15 wt%.

The forms of active components present in heterogeneous catalysts are of importance to catalysis. A great many oxides can disperse spontaneously onto the surfaces of supports to form a monolayer, because the monolayer is a thermodynamically stable form.⁵⁷ When the loading amounts of WO₃ are low, the highly dispersed tungsten oxide species can not be detected by XRD, as shown in Figure 4. Therefore, we can estimate the states of dispersed WO₃ by the XRD analysis. Dispersed WO₃ amount, surface area, acid amount, and catalytic activity for 20NiO/5Al₂O₃-TiO₂/WO₃ catalysts containing different WO₃ contents below 20 wt% are listed in Table 3. There are good correlations among the

dispersed WO₃ amount, acidity, and catalytic activity. Namely, the larger the dispersed WO₃ amount, the higher both the acidity and the catalytic activity. This can be explained by the suggestion that strong acid sites are formed through the bonding between dispersed WO₃ and TiO₂ and consequently catalytic activity increases due to the increased acid sites.

The acid strength of the catalysts was examined by a color change method, using Hammett indicator^{32,39} in sulphuryl chloride. The 5NiO/5Al₂O₃-TiO₂/15WO₃ sample after evacuation at 500 °C for 1 h was estimated to have H₀ ≤ -14.5, indicating the formation of superacidic sites. Acids stronger than H₀ ≤ -11.93, which corresponds to the acid strength of 100% H₂SO₄, are superacids.⁵⁸ Consequently, NiO/Al₂O₃-TiO₂/WO₃ catalysts would be solid superacids. The superacidic property is attributed to the double bond nature of the W=O in the complex formed by the interaction of TiO₂ with tungstate, in analogy with the case of ZrO₂ modified with chromate and sulfate ions.^{18,59}

Effect of Al₂O₃ addition on catalytic activity. The catalytic activity of 20NiO/Al₂O₃-TiO₂/15WO₃ as a function of Al₂O₃ content for ethylene dimerization was examined,

**Figure 9.** Catalytic activity of 20NiO/Al₂O₃-TiO₂/15WO₃ at 20 °C as a function of Al₂O₃ content.

where the catalysts were pretreated at 400 °C for 1 h before reaction; the results are shown in the Figure 9. The catalytic activity increased with increasing the Al₂O₃ content, reaching a maximum at 5 mol%.

Considering the experimental results of Table 2 and Figure 9, it seems likely that the catalytic activity closely relates to the change of acidity of catalysts. As listed in Table 3, the total acid sites of 20NiO/5Al₂O₃-TiO₂/15WO₃ and 20NiO/TiO₂/15WO₃ are 247 μmol/g and 182 μmol/g, respectively, showing that the number of acid sites for the catalyst promoted with Al₂O₃ is greater than that for nonpromoted catalyst. This is consistent with the results reported by Hua *et al.* over Al₂O₃-promoted SO₄²⁻/ZrO₂.⁴⁵ Al₂O₃-promoted catalysts could be related to a strong interaction between Al₂O₃ and TiO₂. Since the promoting effect of Al₂O₃ is related to an increase in number of surface acidic sites, it would be of interest to examine various factors influencing the enhancement of these surface acidic sites.

Xia *et al.*⁶⁰ proposed that Al₂O₃ incorporation in TiO₂ matrix brought about an increase of the positive partial charge on the Ti cations as a result of the formation of Al-O-Ti bonds which helped to stabilize the sulfate species at the oxide surface. The formation of Al-O-Ti bond on the surface of the Al₂O₃-promoted catalysts is probably the cause for the increase in strong acidic sites. According to the principle of electronegativity equalization proposed by Sanderson,⁶¹ since the electronegativity of Al³⁺ is larger than that of Ti⁴⁺, the positive charge on Ti atom is increased as a result of the formation of Al-O-Ti bond, which generates stronger acidity on these sites.⁴⁵ At the same time, the stronger Al-O-Ti bond formed by the charge transfer from Ti atom to neighboring Al atom results in an increase in the thermal stability of the surface tungstate species and consequently the acidity of Al₂O₃-promoted catalyst is increased.

Catalytic activity as a function of NiO content. The catalytic activity of NiO/5Al₂O₃-TiO₂/15WO₃ containing different NiO contents was examined; the results are shown as a function of NiO content in Figure 10. Catalysts were evacuated at 400 °C for 1 h before each reaction. The catalytic activity gives a maximum at 20 wt % of NiO. This seems to be correlated to the specific surface area and to the acidity of catalysts. The acidity of NiO/5Al₂O₃-TiO₂/15WO₃ calcined at 400 °C was determined by the amount of NH₃ irreversibly adsorbed at 230 °C.³⁷⁻³⁹ As mentioned above, the BET surface area attained a maximum extent when the NiO content in the catalyst was 20 wt % and then showed a gradual decrease with increasing NiO content due to the blocking of TiO₂ pore by the increased NiO loading. It has been suggested that the active site for dimerization is formed by an interaction of a low-valent nickel ion with an acid site.^{9,13} Therefore, as shown in Figure 10, 5Al₂O₃-TiO₂/15WO₃ without NiO did not exhibit catalytic activity for ethylene dimerization absolutely. In fact, nickel oxide, which is active for C₂H₄-C₂D₄ equilibration, acquires an activity for ethylene dimerization upon addition of nickel sulfate, which is known to be an acid.¹⁴ The presence of NiO may attract reactants and enhance the local concentration of

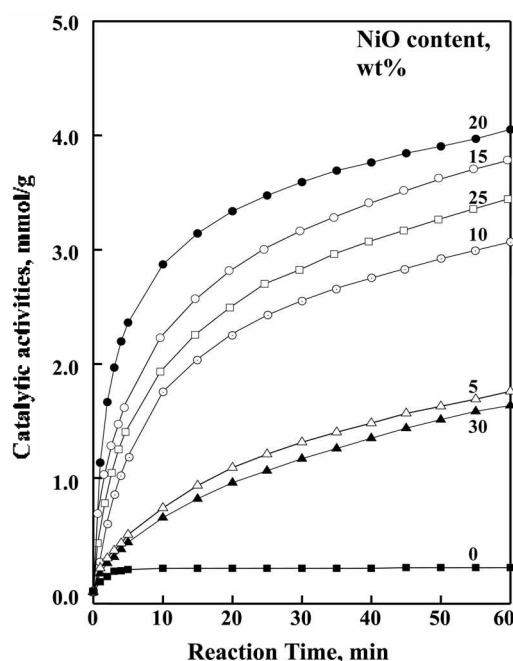


Figure 10. Catalytic activity of NiO/5Al₂O₃-TiO₂/15WO₃ at 20 °C as a function of NiO content.

reactants near acid sites,⁴⁸ consequently showing the increased catalytic activity. In view of Table 1 and Figure 10, the higher the acidity, the higher the catalytic activity. Good correlations have been found in many cases between the acidity and the catalytic activities of solid acids. For example, the rates of both the catalytic decomposition of cumene and the polymerization of propylene over SiO₂-Al₂O₃ and supported NiO catalysts were found to increase with increasing acid amount at strength H₀ ≤ +3.3.⁶² The catalytic activity of nickel-containing catalysts in ethylene dimerization as well as in butene isomerization is closely correlated with the acidity of the catalyst.^{4,8,46,53}

Conclusions

Strong solid acid catalysts, NiO/Al₂O₃-TiO₂/WO₃ were prepared by adding Al₂O₃ to TiO₂ and modifying TiO₂ with WO₃ for ethylene dimerization. 20NiO/5Al₂O₃-TiO₂/15WO₃ containing 20 wt % NiO, 15 wt% WO₃ and 5 mol % Al₂O₃, and calcined at 400 °C, exhibited maximum catalytic activity for ethylene dimerization. The strong acid sites were by the inductive effect of WO₃ species formed through the bonding between dispersed WO₃ and TiO₂. The larger the dispersed WO₃ amount, the higher both the acidity and catalytic activity. The addition of Al₂O₃ up to 5 mol% enhanced acidity and catalytic activity of NiO/Al₂O₃-TiO₂/WO₃ gradually due to the interaction between Al₂O₃ and TiO₂ and consequent formation of Al-O-Ti bond.

Acknowledgements. This work was supported by 2007 Research Fund of University of Ulsan. We wish to thank Korea Basic Science Institute (Daegu Branch) for the use of their X-ray diffractometer.

References

1. Pae, Y. I.; Lee, S. H.; Sohn, J. R. *Catal. Lett.* **2005**, *99*, 241.
2. Bernardi, F.; Bottoni, A.; Rossi, I. *J. Am. Chem. Soc.* **1998**, *120*, 7770.
3. Sohn, J. R.; Ozaki, A. *J. Catal.* **1979**, *59*, 303.
4. Sohn, J. R.; Ozaki, A. *J. Catal.* **1980**, *61*, 29.
5. Wendt, G.; Fritsch, E.; Schöllner, R.; Siegel, H. Z. *Anorg. Allg. Chem.* **1980**, *467*, 51.
6. Sohn, J. R.; Shin, D. C. *J. Catal.* **1996**, *160*, 314.
7. Berndt, G. F.; Thomson, S. J.; Webb, G. J. *J. Chem. Soc. Faraday Trans.* **1983**, *179*, 195.
8. Sohn, J. R.; Lim, J. S. *Bull. Korean Chem. Soc.* **2005**, *26*, 1029.
9. Sohn, J. R.; Park, W. C.; Kim, H. W. *J. Catal.* **2002**, *209*, 69.
10. Sohn, J. R.; Park, W. C. *Bull. Korean Chem. Soc.* **2000**, *21*, 1063.
11. Urabe, K.; Koga, M.; Izumi, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 807.
12. Wendt, G.; Hentschel, D.; Finster, J.; Schöllner, R. *J. Chem. Soc. Faraday Trans.* **1983**, *179*, 2013.
13. Kimura, K.; Ozaki, A. *J. Catal.* **1964**, *3*, 395.
14. Maruya, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 351.
15. Hartmann, M.; Pöpl, A.; Kevan, L. *J. Phys. Chem.* **1996**, *100*, 9906.
16. Elev, I. V.; Shelimov, B. N.; Kazansky, V. B. *J. Catal.* **1984**, *89*, 470.
17. Choo, H.; Kevan, L. *J. Phys. Chem. B* **2001**, *105*, 6353.
18. Sohn, J. R.; Kim, H. J. *J. Catal.* **1986**, *101*, 428.
19. Sohn, J. R.; Lee, S. Y. *Appl. Catal. A: Gen.* **1997**, *164*, 127.
20. Sohn, J. R.; Kim, H. W.; Park, M. Y.; Park, E. H.; Kim, J. T.; Park, S. E. *Appl. Catal.* **1995**, *128*, 127.
21. Hsu, C. Y.; Heimbuch, C. R.; Armes, C. T.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1645.
22. Cheung, T. K.; Gates, B. C. *J. Catal.* **1997**, *168*, 522.
23. Adeeva, V.; de Haan, H. W.; Janchen, J.; Lei, G. D.; Schunemann, V.; van de Ven, L. J. M.; Sachtler, W. M. H.; van Santen, R. A. *J. Catal.* **1995**, *151*, 364.
24. Wan, K. T.; Khouw, C. B.; Davis, M. E. *J. Catal.* **1996**, *158*, 311.
25. Song, X.; Reddy, K. R.; Sayari, A. *J. Catal.* **1996**, *161*, 206.
26. Coelho, M. A.; Resasco, D. E.; Sikabwe, E. C.; White, R. L. *Catal. Lett.* **1995**, *32*, 253.
27. Hosoi, T.; Shimadzu, T.; Ito, S.; Baba, S.; Takaoka, H.; Imai, T.; Yokoyama, N. *Prepr. Symp. Div. Petr. Chem.*; American Chemical Society: Los Angeles, CA, 1988; p 562.
28. Ebitani, K.; Konishi, J.; Hattori, H. *J. Catal.* **1991**, *130*, 257.
29. Signoretto, M.; Pinna, F.; Strukul, G.; Chies, P.; Cerrato, G.; Ciero, S. D.; Morterra, C. *J. Catal.* **1997**, *167*, 522.
30. Hua, W.; Xia, Y.; Yue, Y.; Gao, Z. *J. Catal.* **2000**, *196*, 104.
31. Moreno, J. A.; Poncelet, G. *J. Catal.* **2001**, *203*, 153.
32. Sohn, J. R.; Cho, E. S. *Appl. Catal. A: Gen.* **2005**, *282*, 147.
33. Sohn, J. R. *J. Ind. Eng. Chem.* **2004**, *10*, 1.
34. Arata, K. *Adv. Catal.* **1990**, *37*, 165.
35. Hino, M.; Arata, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1259.
36. Larsen, G.; Lotero, E.; Para, R. D. In *Proceedings of the 11th International Congress on Catalysis*; Elsevier: New York, 1996; p 543.
37. Sohn, J. R.; Lee, S. G.; Shin, D. C. *Bull. Korean Chem. Soc.* **2006**, *27*, 1623.
38. Sohn, J. R.; Shin, D. C.; Kim, H. W. *J. Ind. Eng. Chem.* **2007**, *13*, 47.
39. Sohn, J. R.; Kwon, S. H.; Shin, D. C. *Appl. Catal. A: Gen.* **2007**, *317*, 216.
40. Sohn, J. R.; Park, M. Y. *Langmuir* **1998**, *14*, 6140.
41. Vuorman, M. A.; Wachs, I. E.; Hirt, A. M. *J. Phys. Chem.* **1991**, *95*, 9928.
42. Cerrato, G.; Marchesea, L.; Marchesea, C. *Appl. Surf. Sci.* **1993**, *70*, 200.
43. Alemany, L. J.; Berti, F.; Busca, G.; Ramis, G.; Robba, D.; Toledo, G. P.; Trombetta, M. *Appl. Catal. B: Environ.* **1996**, *10*, 299.
44. Sohn, J. R.; Cho, S. G.; Pae, Y. I.; Hayashi, S. *J. Catal.* **1996**, *159*, 170.
45. Hua, W.; Xia, Y.; Yue, Y.; Gao, Z. *J. Catal.* **2000**, *196*, 104.
46. Sohn, J. R.; Han, J. S.; Kim, H. W.; Pae, Y. I. *Bull. Korean Chem. Soc.* **2005**, *26*, 755.
47. Sohn, J. R.; Lim, J. S. *Catal. Lett.* **2006**, *108*, 71.
48. Sohn, J. R.; Choi, H. D.; Shin, D. C. *Bull. Korean Chem. Soc.* **2006**, *27*, 821.
49. Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *New Solid Acids and Bases*; Kodansha-Elsevier: Tokyo, 1989; p 185.
50. Sohn, J. R.; Lee, S. H. *Appl. Catal. A: Gen.* **2004**, *266*, 89.
51. Sohn, J. R.; Park, W. C. *Appl. Catal. A: Gen.* **2003**, *239*, 269.
52. Satsuma, A.; Hattori, A.; Mizutani, K.; Furuta, A.; Miyamoto, A.; Hattori, T.; Murakami, Y. *J. Phys. Chem.* **1988**, *92*, 6052.
53. Sohn, J. R.; Han, J. S. *Appl. Catal. A: Gen.* **2006**, *298*, 168.
54. Litteti, L.; Nova, I.; Ramis, G.; Dall'Acqua, L.; Busca, G.; Giamello, E.; Forzatti, P.; Bregani, F. *J. Catal.* **1999**, *187*, 419.
55. Liu, Z.; Chen, Y. *J. Catal.* **1998**, *177*, 314.
56. Zhao, B.; Wang, X.; Ma, H.; Tang, Y. *J. Mol. Catal. A: Chem.* **1996**, *108*, 167.
57. Xie, Y. C.; Tang, Y. Q. *Adv. Catal.* **1990**, *37*, 1.
58. Olah, F. G. A.; Prakash, G. K. S.; Sommer, J. *Science* **1979**, *206*, 13.
59. Sohn, J. R.; Ryu, S. G. *Langmuir* **1993**, *9*, 126.
60. Xia, Y.; Hua, W.; Gao, Z. *Appl. Catal. A: Gen.* **1999**, *185*, 293.
61. Sanderson, R. T. *Chemical Bonds and Bond Energy*; Academic Press: New York, 1976; p 75.
62. Tanabe, K. *Solid Acids and Bases*; Kodansha: Tokyo, 1970; p 103.