

Effect of Dispersed MoO₃ Amount on Catalytic Activity of NiO-ZrO₂ Modified with MoO₃ for Acid Catalysis

Jong Rack Sohn,* Sung Gyu Lee, and Dong Cheol Shin

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

*E-mail: jrsohn@knu.ac.kr

Received July 15, 2006

NiO supported on zirconia modified with MoO₃ for acid catalysis was prepared by drying powdered Ni(OH)₂-Zr(OH)₄ with ammonium heptamolybdate aqueous solution, followed by calcining in air at high temperature. The characterization of prepared catalysts was performed using FTIR, Raman, XRD, and DSC. MoO₃ equal to or less than 15 wt% was dispersed on the surface of catalyst as two-dimensional polymolybdate or monomolybdate, while for MoO₃ above 15 wt%, crystalline orthorhombic phase of MoO₃ was formed, showing that the critical dispersion capacity of MoO₃ on the surface of catalyst is 0.18 g/g NiO-ZrO₂ on the basis of XRD analysis. Acidity and catalytic activities for acid catalysis increased with the amount of dispersed MoO₃. The high acid strength and acidity was responsible for the Mo=O bond nature of the complex formed by the interaction between MoO₃ and ZrO₂. The catalytic activity for acid catalysis was correlated with the acidity of the catalysts measured by the ammonia chemisorption method.

Key Words : NiO-ZrO₂/MoO₃ catalyst, MoO₃ dispersion, Acid catalysis, 2-Propanol dehydration, Cumene dealkylation

Introduction

Supported metal oxides¹⁻³ exhibit interesting catalytic behavior depending on the kind of support, the content of active component, and the preparation method. It is well known that the dispersion, the oxidation state, and the structural features of supported species may strongly depend on the support. Structure and physicochemical properties of supported metal oxides are considered to be different compared with bulk metal oxides because of their interaction with supports.

On the other hand, solid acid catalysts play an important role in hydrocarbon conversion reactions in the chemical and petroleum industries.^{4,5} Many kinds of solid acids have been found, their acidic properties on catalyst surfaces, their catalytic action, and the structure of acid sites have been elucidated for a long time, and those results have been reviewed by Arata.⁶ Zirconium oxide is a very interesting material because of its thermal stability, its mechanical properties and its basic, acidic, reducing, and oxidizing surface properties. Therefore, it is attracting interest in catalysis as a support material as well as a catalyst. The strong acidity of zirconia-supported sulfate has attracted much attention because of its ability to catalyze many reactions such as cracking, alkylation, and isomerization. The potential for a heterogeneous catalyst has yielded many papers on the catalytic activity of sulfated zirconia materials.⁶⁻⁸ 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.^{9,10} Coelho *et al.*¹¹ have discovered that the addition of Ni to sulfated zirconia causes an activity enhancement

comparable to that caused by the addition of Fe and Mn. It has been reported by several workers that the addition of platinum to zirconia modified by sulfate ions enhances the catalytic activity in the skeletal isomerization of alkanes without deactivation when the reaction is carried out in the presence of hydrogen.^{12,13} Recently, it has been found that a main group element Al can also promote the catalytic activity and stability of sulfated zirconia in ethylene dimerization and *n*-butane isomerization.¹⁴⁻¹⁶

Recently, some workers reported zirconia-supported tungsten oxide or molybdenum oxide as alternative materials in reactions requiring strong acid sites.^{6,17-19} Several advantages of tungstate or molybdate, over sulfate, as dopant include the facts that it does not suffer from dopant loss during thermal treatment and that it undergoes significantly less deactivation during catalytic reaction.¹⁷ In this paper, these authors tried to prepare other catalyst systems by combining nickel hydroxide to give nickel oxide after decomposition at high temperatures with ZrO₂ modified by MoO₃ which is known to be an acid,^{19,20} to improve the catalytic activity for acid catalysis. Especially, the effect of dispersed MoO₃ amount on catalytic activity for acid catalysis was emphasized. For the acid catalysis, the 2-propanol dehydration and cumene dealkylation were used as test reactions.

Experimental Section

Catalyst Preparation. 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 coprecipitate thus obtained was washed thoroughly with distilled

water until chloride ion was not detected, and then was dried at 100 °C for 12 h. The dried coprecipitate was powdered below 100 mesh.

The catalysts containing various molybdenum oxide contents were prepared by adding an aqueous solution of ammonium heptamolybdate $[(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24})\cdot 4\text{H}_2\text{O}]$ to the $\text{Ni}(\text{OH})_2\text{-Zr}(\text{OH})_4$ 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 MoO_3 . For example, 10-NiO-ZrO₂/15-MoO₃ indicates the catalyst containing 10 wt % NiO regarding only two components, NiO and ZrO₂, and containing 15 wt % MoO₃ regarding all three components, NiO, ZrO₂ and MoO₃.

Procedure. 2-Propanol dehydration was carried out at 160 and 180 °C in a pulse micro-reactor connected to a gas chromatograph. Fresh catalyst in the reactor made of 1/4 in. stainless steel was pretreated at 400 °C for 1 h in a nitrogen atmosphere. Diethyleneglycol succinate on Shimalite was used as packing material of the gas chromatograph and the column temperature for analyzing the product was 150 °C. Catalytic activity for 2-propanol dehydration was represented as mol of propylene converted from 2-propanol per gram of catalyst. Cumene dealkylation was carried out at 400 and 450 °C in the same reactor as above. Packing material for the gas chromatograph was Bentone 34 on Chromosorb W and column temperature was 130 °C. Catalytic activity for cumene dealkylation was represented as mol of benzene converted from cumene per gram of catalyst. The average of the first to sixth pulse values were taken as the conversions for both reactions.

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 the samples under vacuum at 500 °C for 1.5 h.

The Raman spectra were recorded on a Spex Ramalog spectrometer with holographic gratings. The 5145-Å line from a Spectra-Physics Model 165 argon-ion laser was used as the exciting source. The spectral shift width was typically 4 cm⁻¹, and laser source powers of approximately 45 mW, measured at the sample, were used.

Catalysts were checked in order to determine the structure of the support as well as that of molybdenum oxide by means of a Jeol Model JDX-8030 diffractometer, employing Cu K α (Ni-filtered) radiation.

DSC measurements were performed by a PL-STA model 1500H apparatus in air, and the heating rate was 5 °C per minute. For each experiment, 10-15 mg of sample was used.

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 each catalyst. The amount of chemisorption was determined based on the irreversible adsorption of ammonia.²¹⁻²³

Results and Discussion

Crystalline Structures of Catalysts. The crystalline

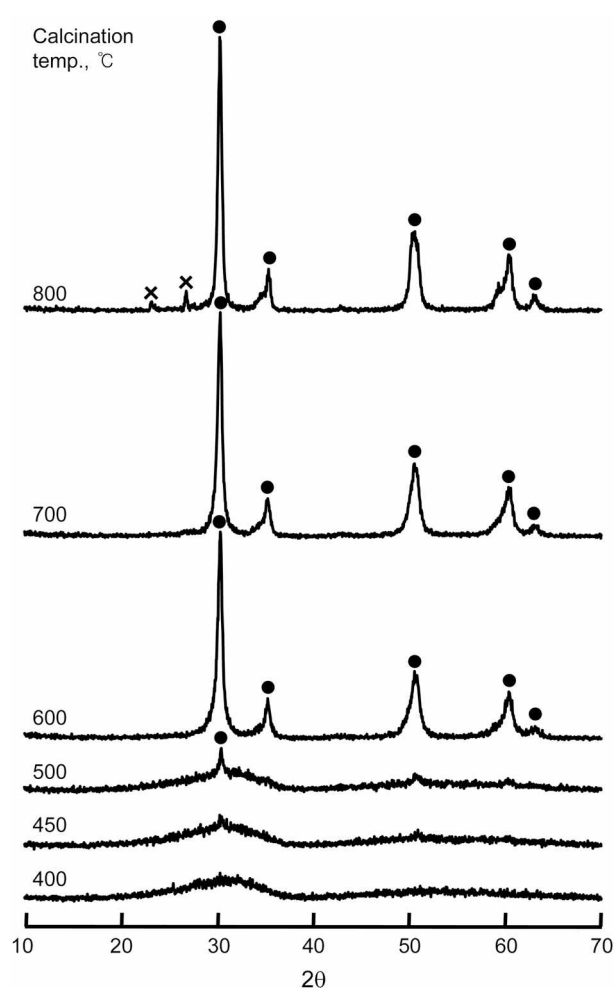


Figure 1. X-ray diffraction patterns of 10-NiO-ZrO₂/15-MoO₃ calcined at different temperatures for 1.5 h: ●, tetragonal ZrO₂; ×, orthorhombic MoO₃.

structures of ZrO₂ and NiO-ZrO₂/MoO₃ calcined in air at different temperatures for 1.5 h were examined. For pure ZrO₂, ZrO₂ was amorphous to X-ray diffraction up to 300 °C, with a two-phase mixture of the tetragonal and monoclinic forms at 400-700 °C and a monoclinic form at 800 °C (This figure is not shown here). Three crystal structures of ZrO₂, tetragonal, monoclinic and cubic phases have been reported.^{24,25} However, in the case of NiO-ZrO₂ modified with MoO₃, the crystalline structures of the samples were different from that of pure ZrO₂. For the 10-NiO-ZrO₂/15-MoO₃, as shown in Figure 1, ZrO₂ was amorphous to X-ray diffraction up to 500 °C with tetragonal ZrO₂ form at 600-800 °C. The transition temperature of ZrO₂ from amorphous to tetragonal phase was higher by 200 °C than of pure ZrO₂. However, the higher the calcination temperature, the larger the amount of tetragonal phase of ZrO₂. It is assumed that the interaction between molybdenum oxide (or NiO) and ZrO₂ hinders the transition of ZrO₂ from amorphous to tetragonal phase.^{26,27} The presence of molybdenum oxide strongly influences the development of textural properties with temperature. No phase of molybdenum oxide or nickel oxide was observed at any calcination temperature, indicat-

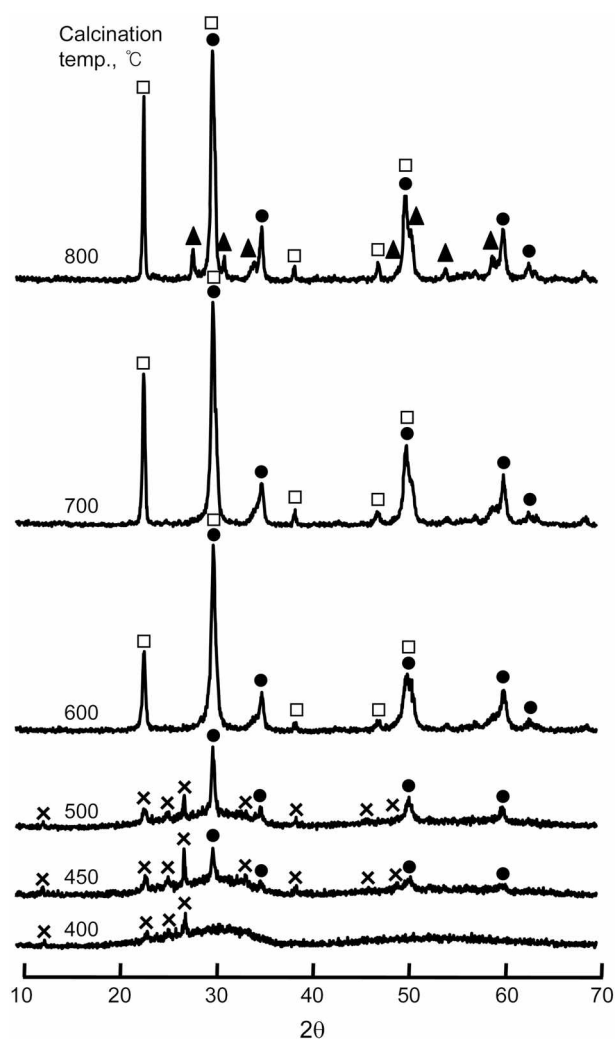


Figure 2. X-ray diffraction patterns of 10-NiO-ZrO₂/25-MoO₃ calcined at different temperatures for 1.5 h: ●, tetragonal ZrO₂; ▲, monoclinic ZrO₂; ×, orthorhombic MoO₃; □, hexagonal Mo(ZrO₄)₂.

ing a good dispersion of molybdenum oxide or nickel oxide on the surface of ZrO₂ support due to the interaction between them.

XRD patterns of 10-NiO-ZrO₂/25-MoO₃ calcined at 400–800 °C for 1.5 h are shown in Figure 2. X-ray diffraction data indicated the amorphous phase of ZrO₂ at 400 °C, showing the tetragonal phase of ZrO₂ at 450–800 °C. However, the higher the calcined temperature, the larger the amount of tetragonal phase of ZrO₂. Moreover, as shown in Figure 2, the orthorhombic phase of MoO₃ was observed at 400–500 °C. It has been reported that MoO₃ for samples containing low MoO₃ loading is dispersed on the surface of zirconia as a monolayer state,^{28,29} that is, two-dimensional polymolybdate or monomolybdate, which gives rise to the characteristic broad band at 900–1000 cm⁻¹. However, when MoO₃ loading exceeds a monolayer capacity on the surface of NiO-ZrO₂, the residual crystalline phase of MoO₃ can be detected by XRD, Raman, and IR. From the calcination temperature of 600 °C, a new species, i.e., Zr(MoO₄)₂ hexagonal phase, has been detected in the 10-NiO-ZrO₂/25-MoO₃

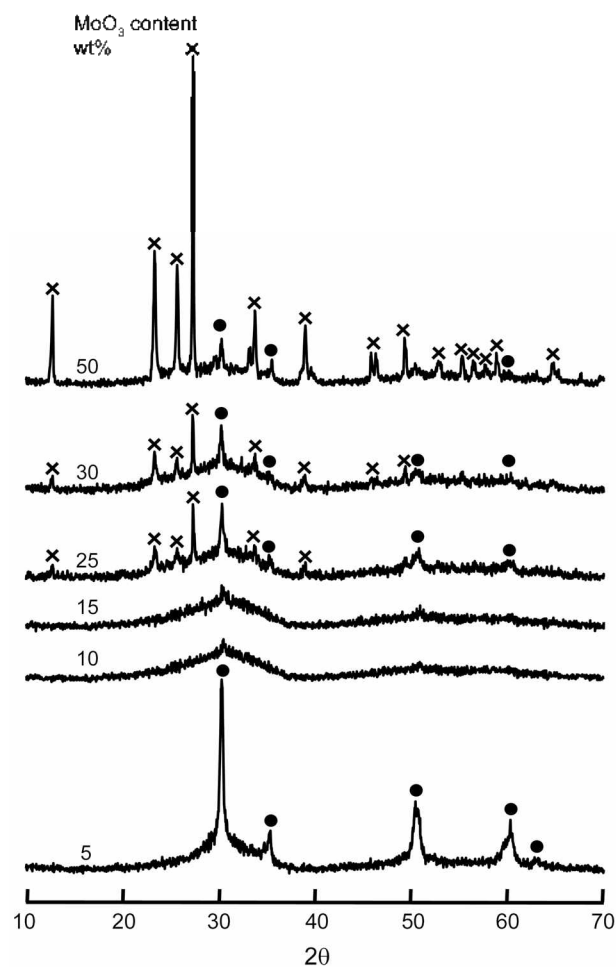


Figure 3. X-ray diffraction patterns of 10-NiO-ZrO₂/MoO₃ containing different MoO₃ contents and calcined at 450 °C for 1.5 h: ●, tetragonal ZrO₂; ×, orthorhombic MoO₃.

catalyst. As shown in Figure 2, the amount of Zr(MoO₄)₂ phase increased with the calcination temperature. Chen *et al.*³⁰ reported the formation of Zr(MoO₄)₂ from MoO₃ and ZrO₂ in high MoO₃ loading sample calcined above 600 °C.

The XRD patterns of 10-NiO-ZrO₂/MoO₃ containing different MoO₃ contents and calcined at 450 °C for 1.5 h are shown in Figure 3. XRD data indicated only tetragonal phase of ZrO₂ at 5 wt% of MoO₃. However, 10-NiO-ZrO₂/10-MoO₃ and 10-NiO-ZrO₂/15-MoO₃ were amorphous to X-ray diffraction, indicating that the increase of MoO₃ loading hinders the phase transition of ZrO₂ from amorphous to tetragonal due to the interaction between MoO₃ and ZrO₂.^{16,27} In this case, no detection of orthorhombic phase of MoO₃ means that all MoO₃ is highly dispersed on the surface of NiO-ZrO₂ as two-dimensional polymolybdate or monomolybdate. For the samples containing higher MoO₃ loading than 15 wt%, as shown in Figure 3, the orthorhombic phase of MoO₃ was observed because MoO₃ loading exceeds a monolayer capacity on the surface of ZrO₂, showing that its intensity increases with the MoO₃ content.

When the loading amounts of MoO₃ are low, the highly dispersed molybdenum oxide species can not be detected by

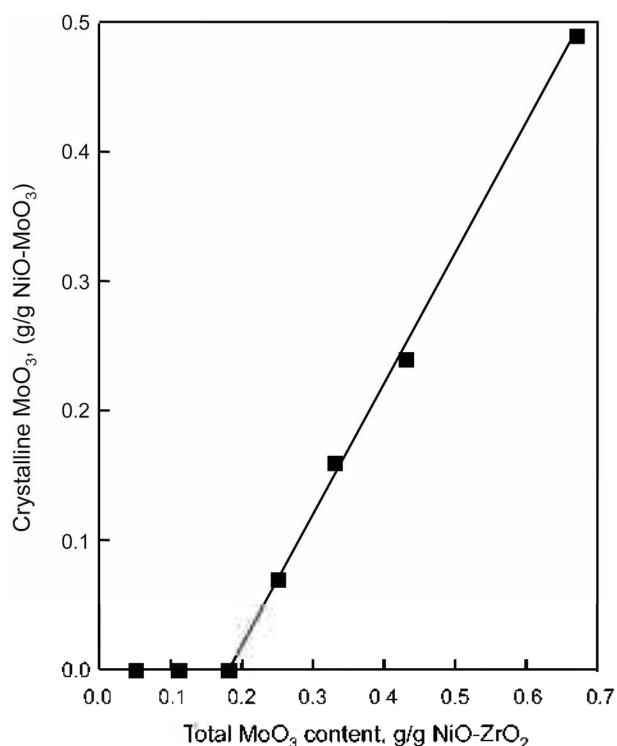


Figure 4. Amount of crystalline MoO₃ against total amount of MoO₃ in 10-NiO-ZrO₂/MoO₃ catalysts containing different MoO₃ contents and calcined at 450 °C for 1.5 h.

XRD, as shown in Figure 3. Therefore, we can estimate the amount of crystalline MoO₃ by the quantitative XRD analysis. Thus, as shown in Figure 4, we can plot the content of crystalline MoO₃ as a function of the total content of MoO₃ in the 10-NiO-ZrO₂/MoO₃ samples containing different MoO₃ contents and calcined at 450 °C, from which the MoO₃ critical dispersion capacity on NiO-ZrO₂, 0.18 g MoO₃/g NiO-ZrO₂ is deduced. Since the surface area of 10-NiO-ZrO₂/15-MoO₃ is 154 m²/g, this capacity is equivalent to 0.12 g MoO₃/100 m² NiO-ZrO₂, which is very similar with the monolayer capacity for MoO₃ supported on ZrO₂.²⁹ It is expected that this dispersion capacity is related to the surface area and acidity of catalysts as discussed below.

Raman and Infrared Spectra. Raman spectroscopy is a valuable tool for the characterization of dispersed metal oxides and detects vibrational modes of surface and bulk structures. The Raman spectra of MoO₃ obtained by calcining ammonium heptamolybdate at 450 °C and 10-NiO-ZrO₂/MoO₃ containing different MoO₃ contents under ambient conditions are presented in Figure 5. The MoO₃ structure is made up of distorted MoO₃ octahedra. Bulk crystalline MoO₃ shows the main bands, in good agreement with data previously reported³¹ and with data of XRD in Figure 2. The major vibrational modes of MoO₃³¹ are located at 995, 819, 667, and 290 cm⁻¹, and have been assigned to the Mo=O stretching mode, the Mo-O-Mo stretching mode, OM₃ vibration mode, and the Mo=O deformation mode, respectively.

The molecular structure of the supported molybdenum

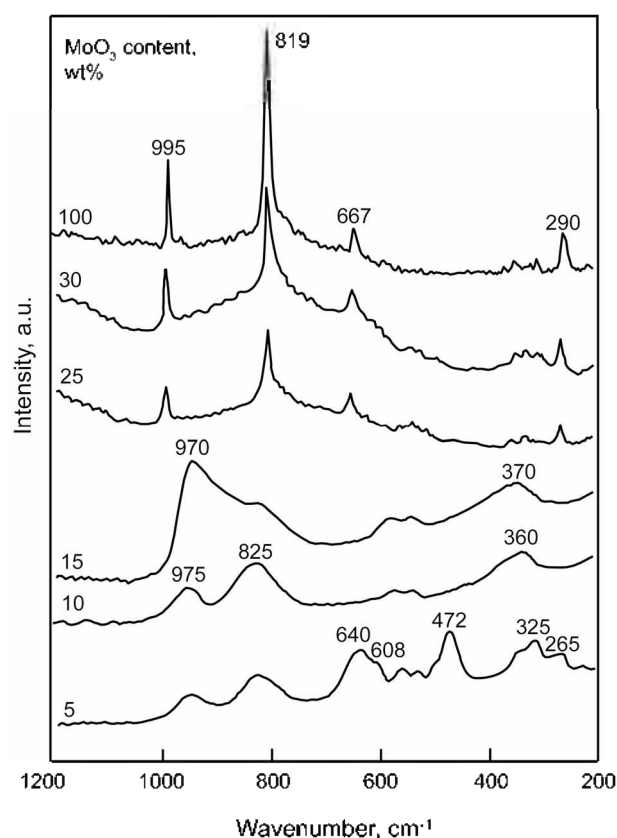


Figure 5. Raman spectra of 10-NiO-ZrO₂/MoO₃ containing different MoO₃ contents and calcined at 450 °C.

oxide species depends on the loading. Several authors observed that the nature of surface molybdenum species on SiO₂, Al₂O₃, TiO₂ and ZrO₂ depends on the amount of MoO₃. A band at about 825 cm⁻¹, corresponding to Mo-O-Mo vibrations,^{28,32} and a band at 910-980 cm⁻¹, assigned to Mo=O vibrations in two-dimensional polymolybdate, were observed in these samples.^{28,32} Raman bands between 910 and 980 cm⁻¹ are usually attributed to the Mo=O vibration of Mo species in either octahedral or tetrahedral environment.³³ Generally, monomolybdate or tetrahedral molybdenum oxygen species have been assigned for low MoO₃ loading samples,^{28,33,34} and two-dimensional polymolybdate or octahedral molybdenum-oxygen species with characteristic band around 950-980 cm⁻¹, for high MoO₃ loading samples.^{28,33,34} Therefore, the broad band observed in the 900-1000 cm⁻¹ region in Figure 5 will be interpreted as an overlap of two characteristic bands for two molybdenum oxide species. The bands around 350-370 cm⁻¹ for 10-NiO-ZrO₂/15-MoO₃ and 10-NiO-ZrO₂/10-MoO₃ samples are assigned to Mo=O bending mode.³⁵

For 10-NiO-ZrO₂/10-MoO₃ and 10-NiO-ZrO₂/15-MoO₃ in Figure 5, most of zirconia is amorphous to X-ray diffraction, showing tiny amount of tetragonal phase zirconia for the other. The Raman spectrum of amorphous zirconia³⁶ is characterized by a very weak and broad band at 550-600 cm⁻¹. Tetragonal zirconia^{37,38} is expected to yield a spectrum consisting of Raman bands with frequencies at about 148,

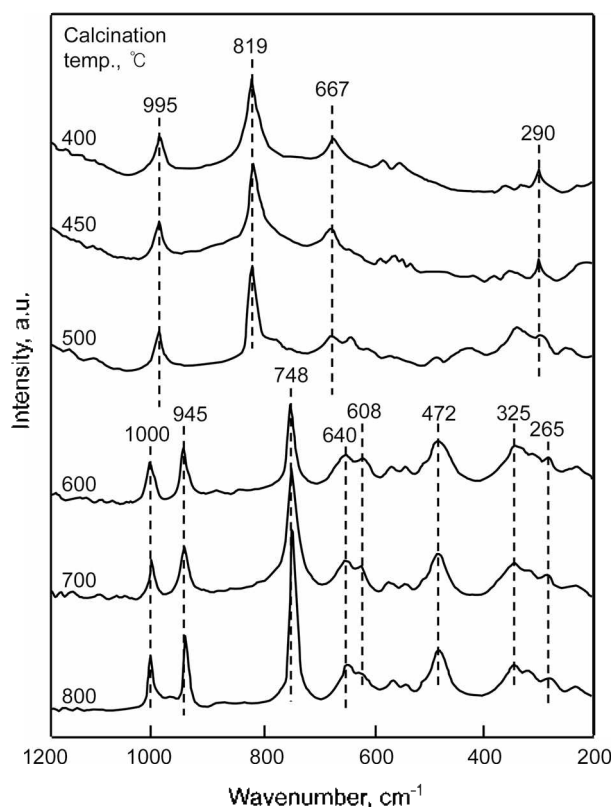


Figure 6. Raman spectra of 10-NiO-ZrO₂/25-MoO₃ calcined at different temperatures for 1.5 h.

263, 325, 472, 608, and 640 cm⁻¹, while monoclinic zirconia^{37,38} exhibits the characteristic features at 180, 188, 221, 380, 476, and 637 cm⁻¹. As shown in Figure 5, the 10-NiO-ZrO₂/5-MoO₃ sample exhibits the characteristic features of tetragonal zirconia, indicating no transformation of ZrO₂ from tetragonal to monoclinic.

Figure 6 shows Raman spectra of 10-NiO-ZrO₂/25-MoO₃ samples calcined at 400–800 °C for 1.5 h. For sample calcined at 400–500 °C, the vibrational modes of bulk MoO₃ were observed at 995, 819, 667 and 290 cm⁻¹ similarly to those of Figure 5. All samples calcined at 450–800 °C except 400 °C also exhibit the characteristic features of tetragonal zirconia at 265, 325, 472, 608, and 640 cm⁻¹, in good agreement with XRD data described above. However, from calcination temperature of 600 °C, a new species, *i.e.*, Zr(MoO₄)₂ phase, identified by its characteristic Raman bands²⁸ at 748, 945, and 1000 cm⁻¹, has been detected in the 10-NiO-ZrO₂/25-MoO₃ catalyst. As shown in Figure 6, the amount of Zr(MoO₄)₂ phase increased with the calcination temperature. Chen *et al.*³⁰ reported the formation of Zr(MoO₄)₂ from MoO₃ and ZrO₂ in high loading sample calcined above 600 °C.

Figure 7 shows IR spectra of 10-NiO-ZrO₂/MoO₃ catalysts (KBr disc) with different MoO₃ contents calcined at 450 °C for 1.5 h. Although with samples having less than 20 wt% of MoO₃ no definite peaks were observed, the absorption bands at 994, 862, and 599 cm⁻¹ appeared for 10-NiO-ZrO₂/MoO₃ having more than 15 wt% of MoO₃. These bands are due to

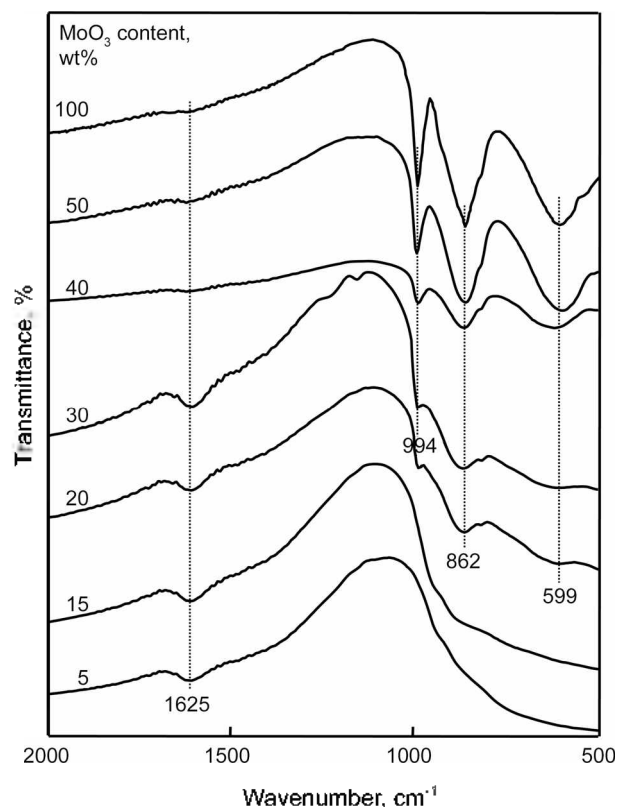


Figure 7. Infrared spectra of 10-NiO-ZrO₂/MoO₃ containing different MoO₃ contents and calcined at 450 °C for 1.5 h.

the crystalline MoO₃. When MoO₃ loading exceeds a certain value, the surplus MoO₃ is present as crystalline form.^{28,29,39} In view of Raman spectra of crystalline MoO₃ in Figure 5, for crystalline MoO₃ the IR bands at 991, 870, and 596 cm⁻¹ in Figure 7 are assigned to the Mo=O stretching mode, the Mo-O-Mo stretching mode, and OMo₃ vibration mode, respectively. XRD measurements have also supported the presence of the above crystalline MoO₃, as discussed above.

The Raman and IR spectra in Figures 5–7 have been taken in air using the pure powders. To examine the structure of NiO-ZrO₂ modified with MoO₃ under dehydration conditions, IR spectra of 10-NiO-ZrO₂/15-MoO₃ sample were obtained in a heatable gas cell after evacuation at 25 and 500 °C for 1.5 h (This figure is not shown here). For 10-NiO-ZrO₂/15-MoO₃ sample, IR band at 997 cm⁻¹ after evacuation at 500 °C is due to the Mo=O stretching mode of the molybdenum oxide complex bonded to the ZrO₂ surface.⁴⁰ This Mo=O band due to molybdenyl species only appears on evacuated sample, being shifted on wet sample. The broad band at 944 cm⁻¹ under ambient condition is assigned to the terminal Mo=O stretching of the hydrated form of the surface molybdenyl species.⁴⁰ This can be rationalized by assuming that the adsorption of water causes a strong perturbation of the corresponding molybdenum oxide species, with a consequent strong broadening and shift down of this band. This isolated molybdenum oxides species is stabilized through multiple Mo-O-Zr bonds between each molybdenum oxide species and the zirconia surface.^{28,30} Upon dehydration at

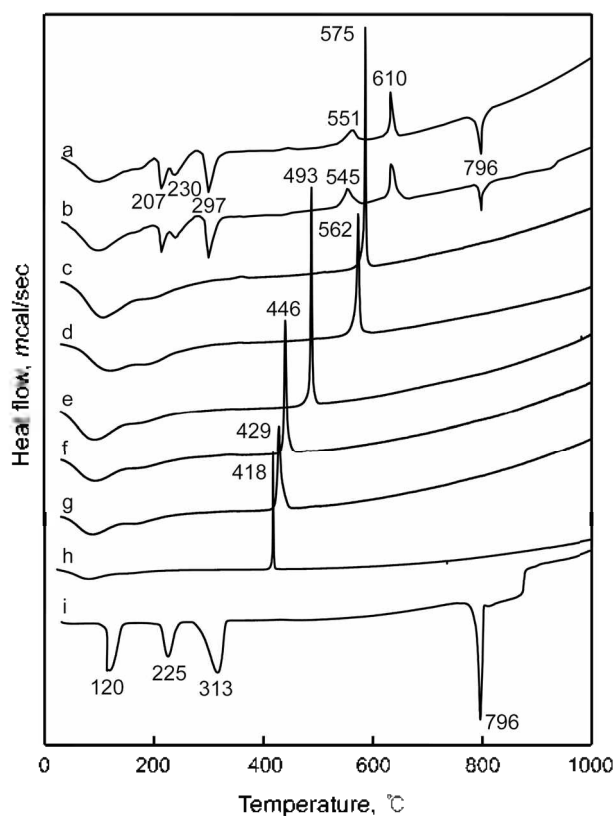


Figure 8. DSC curves of catalyst precursors: (a) 10-NiO-ZrO₂/25-MoO₃, (b) ZrO₂/15-MoO₃, (c) 25-NiO-ZrO₂, (d) 17-NiO-ZrO₂, (e) 10-NiO-ZrO₂, (f) 5-NiO-ZrO₂, (g) 3-NiO-ZrO₂, (h) ZrO₂, and (i) (NH₄)₆(Mo₇O₂₄)·4H₂O.

elevated temperature, the hydrated surface metal oxide species is unstable and decompose to form dehydrated surface metal oxide species by direct interaction with the surface OH groups of support, giving the formation of metal-oxygen-support bond.

Thermal Analysis. In X-ray diffraction pattern, it was shown that the structure of NiO-ZrO₂/MoO₃ was different depending on the calcined temperature. To examine the thermal properties for the precursors of samples more clearly, their thermal analysis was carried out and illustrated in Figure 8. For pure ZrO₂ the DSC curve showed a broad endothermic peak below 180 °C due to the elimination of adsorbed water, and an exothermic peak at 418 °C due to the ZrO₂ crystallization.^{27,37} For (NH₄)₆(Mo₇O₂₄)·4H₂O, the DSC curve shows three endothermic peaks below 400 °C, indicating that the decomposition of ammonium heptamolybdate occurs in three steps. In the case of NiO-ZrO₂/MoO₃, three additional endothermic peaks appeared in the region of 200–400 °C due to the evolution of NH₃ and H₂O decomposed from ammonium heptamolybdate. Also it is considered that an endothermic at 796 °C is responsible for melting of MoO₃³⁹ and an exothermic peak around 610 °C is due to the formation of Zr(MoO₄)₂ described in X-ray diffraction patterns. However, it is of interest to see the influence of NiO and MoO₃ on the crystallization of ZrO₂ from amorphous to tetragonal phase. As Figure 8 shows, the exothermic

Table 1. Specific surface area and acidity of 10-NiO-ZrO₂/MoO₃ catalysts containing different MoO₃ contents and calcined at 450 °C for 1.5 h

MoO ₃ content (wt %)	Surface area (m ² /g)	Acidity (μmol/g)
5	128	112
10	140	134
15	155	141
20	138	129
25	124	121

Table 2. Specific surface area and acidity of NiO-ZrO₂/15-MoO₃ catalysts containing different NiO contents and calcined at 450 °C for 1.5 h

NiO content (wt %)	Surface area (m ² /g)	Acidity (μmol/g)
3	139	78
5	143	119
10	155	141
15	138	137
20	128	121
30	121	95
40	89	78

peak due to the crystallization appears at 418 °C for pure ZrO₂, while for NiO-ZrO₂ and NiO-ZrO₂/MoO₃, it was shifted to higher temperatures. The shift increased with increasing NiO content up to 25 wt% of NiO. It is considered that the interaction between NiO (or MoO₃) and ZrO₂ delays the transition of ZrO₂ from amorphous to tetragonal phase.¹⁶ Consequently, the exothermic peaks appear at 429 °C for 3-NiO-ZrO₂, 446 °C for 5-NiO-ZrO₂, 493 °C for 10-NiO-ZrO₂, 545 °C for ZrO₂/15-MoO₃, 551 °C for 10-NiO-ZrO₂/25-MoO₃, 562 °C for 17-NiO-ZrO₂, and 575 °C for 25-NiO-ZrO₂.

Surface Properties. It is necessary to examine the effect of molybdenum oxide on the surface properties of catalysts, that is, specific surface area, acidity, and acid strength. The specific surface areas of 10-NiO-ZrO₂/MoO₃ samples calcined at 450 °C for 1.5 h are listed in Table 1. The presence of molybdenum oxide strongly influences the surface area in comparison with the pure ZrO₂. Specific surface areas of 10-NiO-ZrO₂/MoO₃ samples are much larger than that of pure ZrO₂ calcined at the same temperature, showing that surface area increases gradually with increasing molybdenum oxide content up to 15 wt% of MoO₃. The decrease of surface area for samples containing MoO₃ above 15 wt% is due to the blocking of ZrO₂ pore by the increased MoO₃ loading. It seems likely that the interaction between molybdenum oxide and ZrO₂ protects catalysts from sintering. The acidity of catalysts calcined at 450 °C, as determined by the amount of NH₃ irreversibly adsorbed at 230 °C,^{16,41,42} is also listed in Table 1. The acidity per surface area for these catalysts was calculated to be nearly constant values of 0.9–1.0 μmol/m², indicating that the variation of acidity runs parallel to the change of surface area. We examined the effect of NiO

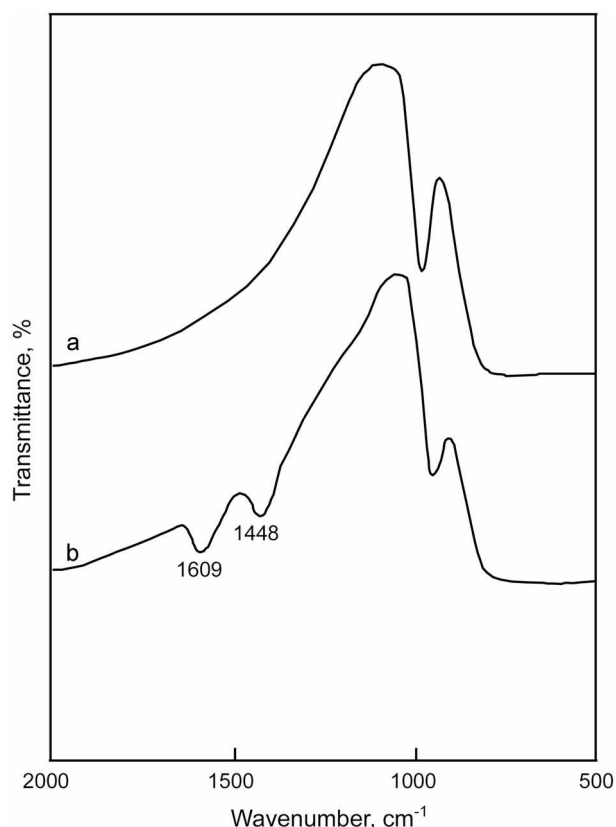


Figure 9. Infrared spectra of NH₃ adsorbed on 10-NiO-ZrO₂/15-MoO₃: (a) background of 10-NiO-ZrO₂/15-MoO₃ after evacuation at 400 °C for 1 h, (b) NH₃ adsorbed on (a); where gas was evacuated at 230 °C for 1 h.

addition on the surface area and acidity of NiO-ZrO₂/15-MoO₃ catalysts. The specific surface areas and acidity of catalysts calcined at 450 °C are listed in Table 2. Both surface area and acidity increased with increasing NiO content up to 10 wt%, indicating the promoting effect of NiO.

The acid strength of the catalysts was examined by a color change method, using Hammett indicator in sulphurylchloride.^{16,19,27} NiO-ZrO₂/MoO₃ was estimated to have a H₀ ≤ -14.5, indicating the formation of new acid sites stronger than those of single oxide components. Acids stronger than H₀ ≤ -11.93, which corresponds to the acid strength of 100% H₂SO₄, are superacids.^{6,43,44} Consequently, NiO-ZrO₂/MoO₃ catalysts would be solid superacids. The superacidic property is attributed to the double bond nature of the Mo=O in the complex formed by the interaction of ZrO₂ with molybdate, in analogy with the case of ZrO₂ modified with tungstate, chromate, and sulfate ions.^{27,45}

Infrared spectroscopic studies of ammonia adsorbed on solid surface have made it possible to distinguish between Brønsted and Lewis acid sites.^{16,19,41} Figure 9 shows the IR spectra of ammonia adsorbed on 10-NiO-ZrO₂/15-MoO₃ evacuated at 400 °C for 1 h. The band at 1448 is the characteristic peak of ammonium ion, which is formed on the Brønsted acid sites and the absorption peak at 1609 cm⁻¹ is contributed by ammonia coordinately bonded to Lewis acid sites,^{16,46,47} indicating the presence of both Brønsted and

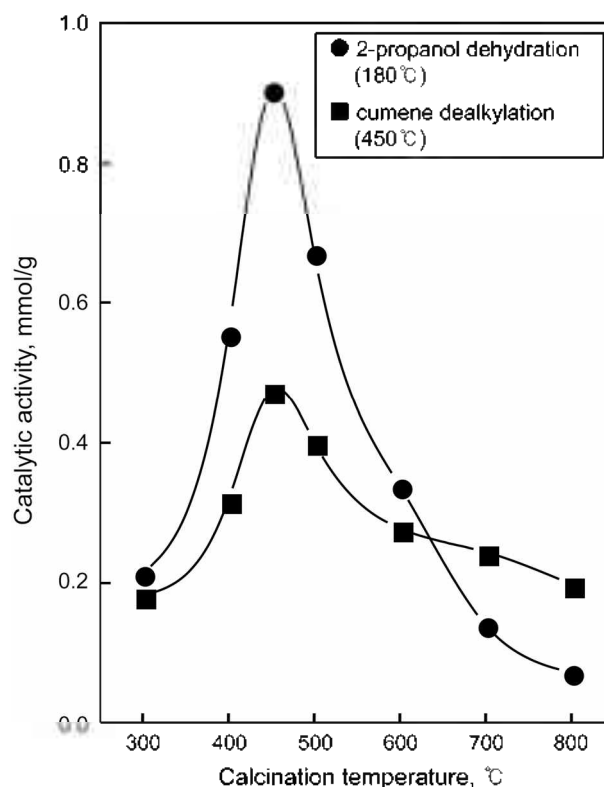


Figure 10. Catalytic activities of 10-NiO-ZrO₂/15-MoO₃ for (●) 2-propanol dehydration (180 °C) and (■) cumene dealkylation as a function of calcination temperature.

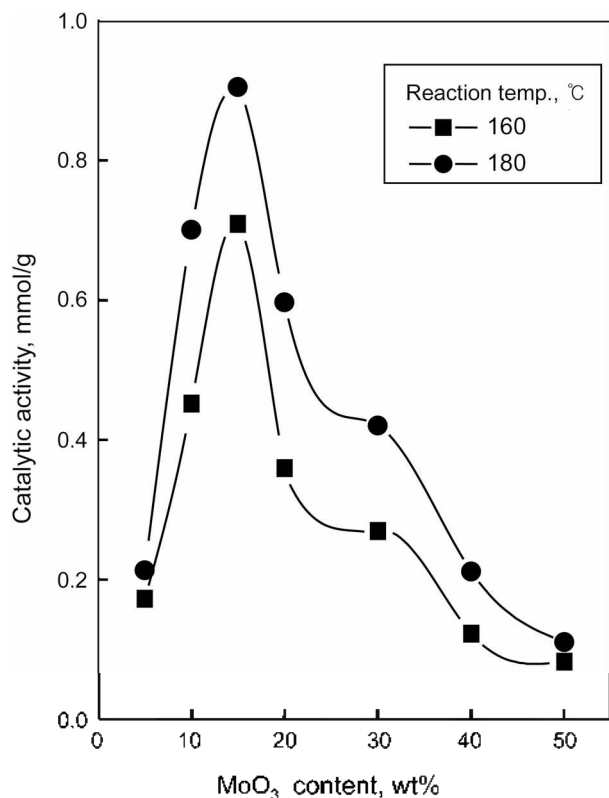
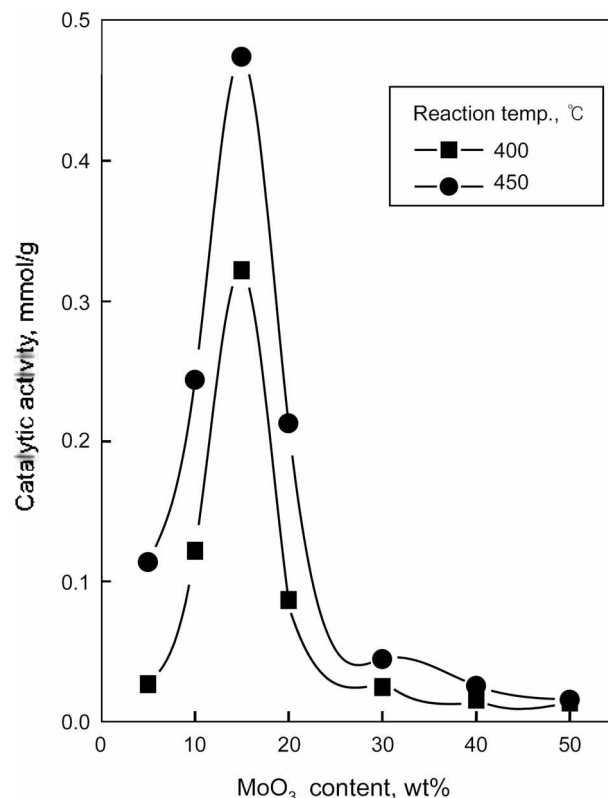
Lewis acid sites on the surface of catalyst. Other samples having different MoO₃ contents also showed the presence of both Lewis and Brønsted acid sites.

Catalytic Activities for Acid Catalysis. Catalytic activities of 10-NiO-ZrO₂/15-MoO₃ for 2-propanol dehydration and cumene dealkylation are plotted as a function of calcination temperature in Figure 10, where reaction temperatures are 180 °C for 2-propanol dehydration and 450 °C for cumene dealkylation, respectively. The activities for both reactions increased with the calcination temperature, reaching a maximum at 450 °C, after which the activities decreased. The decrease of activities for both reactions above 450 °C can be attributed to the fact that the surface area and acidity above 450 °C decrease with the calcination temperature. In fact, the surface area and acidity for 10-NiO-ZrO₂/15-MoO₃ calcined at 450 °C were 154 m²/g and 140 μmol/g, respectively, while those for the catalyst calcined at 800 °C were found to be 45 m²/g and 58 μmol/g, respectively. Thus, hereafter, emphasis is placed only on the catalysts calcined at 450 °C.

Effect of Dispersed MoO₃ Amount on Acidity and Catalytic Activity. The forms of active components present in heterogeneous catalysts are of importance to catalysis. A great many oxides can disperse spontaneously onto the surface of supports to form a monolayer, because the monolayer is a thermodynamically stable form.³⁹ Dispersed MoO₃ amount, surface area, acidity, and catalytic activity for 10-NiO-ZrO₂/MoO₃ catalysts containing MoO₃ content below 20 wt% are listed in Table 3. There are good correlations

Table 3. Dispersed MoO₃ amount, specific surface area, acidity, and catalytic activity of 10-NiO-ZrO₂/MoO₃ catalysts containing MoO₃ content below 20 wt%

Catalyst	Dispersed MoO ₃ amount (MoO ₃ g/NiO-ZrO ₂ g)	Surface area (m ² /g)	Acidity (μmol/g)	Catalytic activity	
				2-propanol dehydration (mmol/g)	Cumene dealkylation (mmol/g)
10-NiO-ZrO ₂ /5-MoO ₃	0.05	128	112	0.21	0.12
10-NiO-ZrO ₂ /10-MoO ₃	0.11	140	134	0.70	0.24
10-NiO-ZrO ₂ /15-MoO ₃	0.18	154	140	0.92	0.48

**Figure 11.** Catalytic activities of 10-NiO-ZrO₂/MoO₃ for 2-propanol dehydration as a function of MoO₃ content.**Figure 12.** Catalytic activities of 10-NiO-ZrO₂/15-MoO₃ for cumene dealkylation as a function of MoO₃ content.

among the dispersed MoO₃ amount, acidity, and catalytic activity. Namely, the larger the dispersed MoO₃ amount, the higher both acidity and catalytic activity. This can be explained in terms of that strong acid sites are formed through the bonding between dispersed MoO₃ and ZrO₂ and consequently catalytic activity increases due to the increased acid sites.

The catalytic activities for 2-propanol dehydration and cumene dealkylation as a function of MoO₃ content are plotted in Figures 11 and 12, respectively. The maximum activities for both reactions are obtained with the catalyst containing 15 wt% MoO₃, where the amount of dispersed MoO₃ is also maximum. It seems likely that the highest activity of the catalyst containing 15 wt% MoO₃ is related to its acidity and acid strength. The high acid strength and acidity are responsible for the Mo=O bond nature of complex formed by the interaction between MoO₃ and ZrO₂.^{6,19} As discussed in IR spectra, IR spectra of 10-NiO-ZrO₂/15-

MoO₃ sample after evacuation at 500 °C showed the band at 997 cm⁻¹ due to the Mo=O stretching mode of the molybdenum oxide complex bonded to the ZrO₂ surface.⁴⁰ This isolated molybdenum oxide species is stabilized through multiple Mo-O-Zr bonds between each molybdenum oxide species and the zirconia surface.^{28,30} As listed in Tables 1 and 3, the acidity of 10-NiO-ZrO₂/15-MoO₃ is the most among the catalysts. Of course, the acidity of catalysts is related to their specific surface area, as mentioned above. In fact, Tables 1 and 3 show that the specific surface area attained a maximum when the MoO₃ content in 10-NiO-ZrO₂/MoO₃ is 15 wt%. Although the sample without MoO₃ was inactive as acid catalyst, as shown in Figures 11 and 12, the 10-NiO-ZrO₂/MoO₃ with MoO₃ exhibited high catalytic activity for acid catalysis.

Correlation between Catalytic Activity and Acidity. It is interesting to examine how the catalytic activity of acid catalyst depends on the acid property. For both 2-propanol

dehydration and cumene dealkylation reactions NiO-ZrO₂/MoO₃ catalysts calcined at 450 °C exhibited the highest catalytic activities. In view of Table 1 and Figure 11, the variation in catalytic activity for 2-propanol dehydration is correlated with the change of their acidity, showing the highest activity and acidity for 10-NiO-ZrO₂/15-MoO₃. It has been known that 2-propanol dehydration takes place very readily on weak acid sites.^{21,48} 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 catalysts were found to increase with increasing acid amounts at strength $H_0 \leq +3.3$.⁴⁹ The catalytic activities for both reactions, 2-propanol dehydration and cumene dealkylation, were correlated with the acidity of NiSO₄ supported on TiO₂-ZrO₂ measured by an ammonia chemisorption method. It was also reported that the catalytic activity of nickel silicates in the ethylene dimerization as well as in the butene isomerization was closely correlated with the acid amount of the catalyst.^{30,51}

Cumene dealkylation takes place on relatively strong acid sites of the catalysts.^{21,48} Catalytic activity for cumene dealkylation against MoO₃ content is presented in Figure 12, where reaction temperature is 400–450 °C. Comparing Table 1 and Figure 12, the catalytic activity is also correlated with the acidity. The correlation between catalytic activity and acidity holds for both reactions, cumene dealkylation and 2-propanol dehydration, although the acid strength required to catalyze acid reaction is different depending on the type of reactions.^{21,48} As seen in Figures 11 and 12, the catalytic activity for cumene dealkylation, in spite of higher reaction temperature, is lower than that for 2-propanol dehydration.

The acidity of the catalysts can be also correlated to the amount of dispersed MoO₃. As listed in Table 3, the maximum acidity is obtained with the catalyst containing 15 wt% MoO₃, where the amount of dispersed MoO₃ is also maximum. The acidity of NiO-ZrO₂/MoO₃ calcined at 450 °C was determined by the amount of NH₃ irreversibly adsorbed at 230 °C.^{16,41,42} As listed in Tables 1 and 2, the BET surface area and acidity attained a maximum extent for the 10-NiO-ZrO₂/15-MoO₃ catalyst. However, as mentioned above, 2-propanol dehydration takes place very readily on weak acid sites, while cumene dealkylation takes place on relatively strong acid sites.^{21,48} Therefore, it seems likely that the patterns of catalytic activities for both reactions as a function of MoO₃ content are more or less different.

Effect of NiO on Catalytic Activity. To examine the promoting effect of NiO on the catalytic activities, the catalytic activities of NiO-ZrO₂/15-MoO₃ for 2-propanol dehydration and cumene dealkylation are plotted as a function of NiO in Figure 13. For both reactions the catalytic activities increased with increasing NiO content up to 10 wt%, and then decreased. However, in view of Table 2 and Figure 13, the increases of catalytic activities by the addition of NiO seem to be correlated with the acidity of catalysts, because the addition of NiO brought about the increase of acidity as

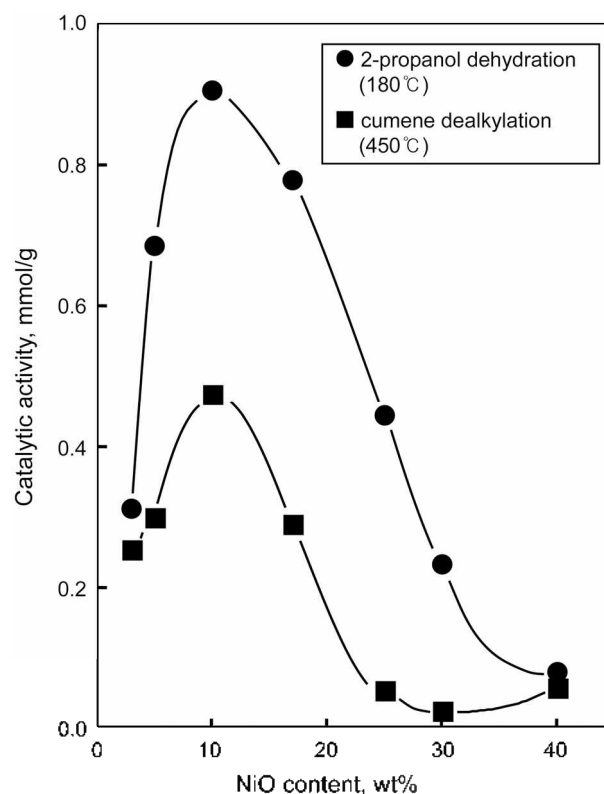


Figure 13. Catalytic activities of NiO-ZrO₂/15-MoO₃ for (●) 2-propanol dehydration and (■) cumene dealkylation as a function of NiO content.

listed in Table 2. The presence of NiO may attract reactants and enhance the local concentration of reactants near the acid sites,³² consequently showing the increased catalytic activities. Conclusively, the addition of NiO (10 wt%) increased not only acidity, but enhanced the concentration of reactants near the acid sites. The high acid strength and high acidity of catalysts modified with MoO₃ are also responsible for the Mo=O bond nature of complex formed by the interaction between dispersed MoO₃ and ZrO₂. Therefore, 10-NiO-ZrO₂/15-MoO₃ exhibited the maximum catalytic activities for acid catalysis.

Conclusions

NiO-ZrO₂/MoO₃ catalysts were prepared by adding an aqueous solution of ammonium metatungstate to the Ni(OH)₂-Zr(OH)₄ powder, followed by drying and calcining at high temperatures for 1.5 h in air. The interaction between molybdenum oxide (or nickel oxide) and zirconia influences the physicochemical properties of prepared catalysts with calcination temperature. The interaction between MoO₃ (or NiO) and ZrO₂ delayed the phase transition of ZrO₂ from amorphous to tetragonal. Since the ZrO₂ stabilizes the surface molybdenum oxide species, for the samples equal to or less than 15 wt%, molybdenum oxide was well dispersed on the surface of zirconia, but for the samples above 15 wt% the orthorhombic phase of MoO₃ was observed at the calcination temperature of 450 °C. The larger the dispersed

MoO₃ amount, the higher both acidity and catalytic activities for acid catalysis, because strong acid sites are formed through the bonding between dispersed MoO₃ and ZrO₂. The high acid strength and high acidity are responsible for the Mo=O bond nature of complex formed by the interaction between MoO₃ and ZrO₂.

Acknowledgement. We wish to thank Korea Basic Science Institute for the use of Raman and X-ray Instruments.

References

1. Wainwright, M. S.; Foster, N. R. *Catal. Rev.* **1979**, *19*, 211.
2. Dadyburjor, D. B.; Jewur, S. S.; Ruckenstein, E. *Catal. Rev.* **1979**, *19*, 293.
3. Sohn, J. R. *J. Ind. Eng. Chem.* **2004**, *10*, 1.
4. Cheung, T. K.; d'Itri, J. L.; Lange, F. C.; Gates, B. C. *Catal. Lett.* **1995**, *31*, 153.
5. Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *New Solid Acids and Bases*; Elsevier Science: Amsterdam, 1989; Chapter 4.
6. Arata, K. *Adv. Catal.* **1990**, *37*, 165.
7. Ward, D. A.; Ko, E. I. *J. Catal.* **1994**, *150*, 18.
8. Kustov, L. M.; Kazansky, V. B.; Figueras, F.; Tichit, D. *J. Catal.* **1994**, *150*, 143.
9. Hsu, C. Y.; Heimbuch, C. R.; Arnes, C. T.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1645.
10. Cheung, T. K.; Gates, B. C. *J. Catal.* **1997**, *168*, 522.
11. Coelho, M. A.; Resasco, D. E.; Sikabwe, E. C.; White, R. L. *Catal. Lett.* **1995**, *32*, 253.
12. 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.
13. Ebitani, K.; Konishi, J.; Hattori, H. *J. Catal.* **1991**, *130*, 257.
14. Hua, W.; Xia, Y.; Yue, Y.; Gao, Z. *J. Catal.* **2000**, *196*, 104.
15. Moreno, J. A.; Poncelet, G. *J. Catal.* **2001**, *203*, 453.
16. Sohn, J. R.; Cho, E. S. *Appl. Catal. A: Gen.* **2005**, *282*, 147.
17. Larsen, G.; Lotero, E.; Parra, R. D. *In Proceeding of the 11th International Congress on Catalysis*; Elsevier: New York, 1996; pp 543-551.
18. Hino, M.; Arata, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1259.
19. Sohn, J. R.; Chun, E. W.; Pae, Y. I. *Bull. Korean Chem. Soc.* **2003**, *24*, 1785.
20. Brown, A. S. C.; Hargreaves, J. S. J.; Taylor, S. H. *Catal. Letts.* **1999**, *57*, 109.
21. Sohn, J. R.; Lee, S. H. *Appl. Catal. A: Gen.* **2004**, *266*, 89.
22. Sohn, J. R.; Han, J. S. *J. Ind. Eng. Chem.* **2005**, *11*, 439.
23. Sohn, J. R.; Han, J. S.; Kim, H. W.; Pae, Y. I. *Bull. Korean Chem. Soc.* **2005**, *26*, 755.
24. Larsen, G.; Lotero, E.; Petkovic, L. M.; Shobe, D. S. *J. Catal.* **1997**, *169*, 67.
25. Afanasiev, P.; Geantet, C.; Breyse, M.; Coudurier, G.; Vadrine, J. C. *J. Chem. Soc., Faraday Trans.* **1994**, *190*, 193.
26. Sohn, J. R.; Kim, Y. T.; Shin, D. C. *Bull. Korean Chem. Soc.* **2005**, *26*, 1479.
27. Sohn, J. R.; Cho, S. G.; Pae, Y. I.; Hayashi, S. *J. Catal.* **1996**, *159*, 170.
28. Liu, Z.; Chen, Y. *J. Catal.* **1998**, *177*, 314.
29. Zhao, B.; Wang, X.; Ma, H.; Tang, Y. *J. Mol. Catal. A: Chem.* **1996**, *108*, 167.
30. Chen, K.; Xie, S.; Iglesia, E.; Bell, A. T. *J. Catal.* **2000**, *189*, 421.
31. Smith, M. R.; Ozkan, U. S. *J. Catal.* **1993**, *141*, 124.
32. Mestl, G.; Srinivasan, T. K. *Cat. Rev. Sci. Eng.* **1998**, *40*, 451.
33. Dufresne, P.; Payen, E.; Grimblot, J.; Bonnelle, J. P. *J. Phys. Chem.* **1981**, *85*, 2344.
34. Hu, H.; Wachs, I. E. *J. Phys. Chem.* **1995**, *99*, 10897.
35. Roark, R. D.; Kohler, S. D.; Ekerdt, J. G.; Kim, D. S.; Wachs, I. E. *Catal. Lett.* **1992**, *16*, 77.
36. Schild, C. H.; Wokaun, A.; Köppel, R. A.; Baiker, A. *J. Catal.* **1991**, *130*, 657.
37. Sohn, J. R.; Doh, I. J.; Pae, Y. I. *Langmuir* **2002**, *18*, 6280.
38. Scheithauer, M.; Grasselli, R. K.; Knözinger, H. *Langmuir* **1998**, *14*, 3019.
39. Xie, Y. C.; Tang, Y. Q. *Adv. Catal.* **1990**, *37*, 1.
40. Litteti, L.; Nova, I.; Ramis, G.; Dall'Acqua, L.; Busca, G.; Giamello, E.; Forzatti, P.; Bregani, F. *J. Catal.* **1999**, *187*, 419.
41. Sohn, J. R.; Lim, J. S. *Catal. Today* **2006**, *111*, 403.
42. Sohn, J. R.; Han, J. S. *Appl. Catal. A: Gen.* **2006**, *298*, 168.
43. Olah, F. G. A.; Prakash, G. K. S.; Sommer, J. *Science* **1979**, *206*, 13.
44. Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *New Solid Acids and Bases*; Elsevier Science: Amsterdam, 1989; p 185.
45. Sohn, J. R.; Ryu, S. G. *Langmuir* **1993**, *9*, 126.
46. Basila, M. R.; Kantner, T. R. *J. Phys. Chem.* **1967**, *71*, 467.
47. Satsuma, A.; Hattori, A.; Mizutani, K.; Furuta, A.; Miyamoto, A.; Hattori, T.; Murakami, Y. *J. Phys. Chem.* **1988**, *92*, 6052.
48. Decanio, S. J.; Sohn, J. R.; Fritz, P. O.; Lunsford, J. H. *J. Catal.* **1986**, *101*, 132.
49. Tanabe, K. *Solid Acids and Bases*; Kodansha: Tokyo, 1970; p 103.
50. Sohn, J. R.; Park, W. C. *Appl. Catal. A: General* **2003**, *239*, 269.
51. Sohn, J. R.; Ozaki, A. *J. Catal.* **1980**, *61*, 29.
52. Pae, Y. I.; Bae, M. H.; Park, W. C.; Sohn, J. R. *Bull. Korean Chem. Soc.* **2004**, *25*, 1881.