

NOTE

New Catalyst of NiO–ZrO₂/WO₃ for Ethylene Dimerization

Nickel oxide on silica or silica–alumina is an effective catalyst for ethylene dimerization and *n*-butene isomerization at room temperature (1–6). 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 (7). In the previous papers from this laboratory, it has been shown that NiO–TiO₂ and NiO–ZrO₂ modified with sulfate ion are very active for ethylene dimerization (8–10). 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 bonds of the complex formed by the interaction of oxides with sulfate ion. As an extension of the study on the ethylene dimerization, we have prepared a new catalyst of NiO–ZrO₂/WO₃ which is active for ethylene dimerization even at room temperature.

The catalysts were prepared as follows. 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 liquid reached about 8. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected, and was dried at 100°C. The precipitate powdered below 100 mesh was impregnated with aqueous ammonium metatungstate [(NH₄)₆(H₂W₁₂O₄₀)·*x*H₂O] followed by evaporating water, drying, and calcining in air at 700°C for 1.5 h. It was used as catalyst after evacuating at different temperatures for 1.5 h. This series of catalysts are denoted by the weight percentage of NiO and WO₃. For example, 25-NiO–ZrO₂/15-WO₃ means the catalyst having 25 wt% of NiO and 15 wt% of WO₃.

The catalytic activity for ethylene dimerization was determined at 20°C by a conventional static system following pressure change from an initial pressure of 300 Torr. Fresh catalyst sample of 0.2 g was used for every run and the catalytic activity was calculated as the amount of ethylene consumed in the initial 5 min. Reaction products were analyzed by gas chromatography with a VZ-7 column at room temperature.

The catalytic activities of NiO–ZrO₂/15-WO₃ for the reaction of ethylene dimerization were examined and the results are shown as a function of NiO content in Fig. 1, where the catalysts were evacuated at 500°C for 1.5 h

before reaction. It is confirmed that the catalytic activity gives a maximum at 25 wt% of NiO and 15 wt% of WO₃. This is due to the increase of specific surface area and the subsequent increase of active sites. As listed in Table 1, the BET surface area attained a maximum when the NiO content in the catalyst is 25 wt%. Although the sample without WO₃ was inactive as catalyst for ethylene dimerization, the NiO–ZrO₂ with WO₃ exhibited high catalytic activity even at room temperature.

The effect of evacuation temperature on the catalytic activity of 25-NiO–ZrO₂/15-WO₃ was also examined, where the catalysts were evacuated for 1.5 h. As shown in Fig. 1, the maximum activity is obtained with the catalyst evacuated at 450°C. To examine the effect of evacuation temperature on surface area, BET surface area of 25-NiO–ZrO₂/15-WO₃ at various evacuation temperature (300–700°C) was measured. However, the particular change of surface area was not observed, giving about 108–114 m²/g regardless of evacuation temperature. Therefore, it seems likely that the variation of catalytic activity is not related to the change of surface area but to the easy formation of active site depending on the evacuation temperature. On all the catalysts of NiO–ZrO₂/WO₃, 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 *cis*-butene and *trans*-butene. However, it was shown that the amount of 1-butene decreases with the reaction time, while the amount of 2-butene increases. Therefore, it seems likely that the initially produced 1-butene is also isomerized to 2-butene during the reaction.

In a previous paper it was demonstrated that the catalytic activities correlate with the acid strengths of the catalysts (9). The acid strength of the present samples was examined by a color change method, using Hammett indicator (11) in sulfuryl chloride. Since it was very difficult to observe the color of indicators adsorbed on the catalyst of high nickel oxide content, the low percentage of nickel oxide (3 wt%) was used in this experiment. The results are listed in Table 2. In this table, + means that the color of base form was changed to that of conjugate acid form. The acid strength of ZrO₂ was found to be $H_o \leq +1.5$, while NiO–ZrO₂ was estimated to have a $H_o \leq -3.0$, indicating the formation of new acid site stronger than those of

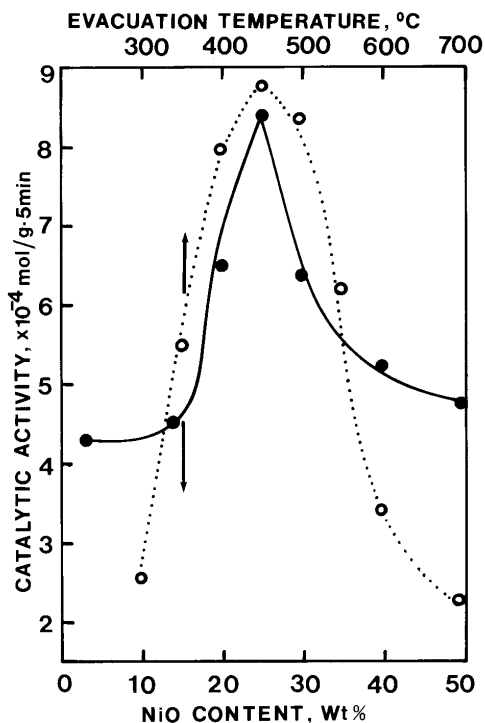


FIG. 1. Variations of catalytic activity for ethylene dimerization with NiO content and evacuation temperature: (●) NiO-ZrO₂/15-WO₃ having different NiO content and evacuated at 500°C; (○) 25-NiO-ZrO₂/15-WO₃ evacuated at different temperature.

single oxide components. The acid strength of ZrO₂/WO₃ and NiO-ZrO₂/WO₃ was also found to be $H_0 \leq -14.5$. An acid stronger than $H_0 = -11.93$, which corresponds to an acid strength of 100% H₂SO₄, is known as a superacid (12). Consequently, ZrO₂/WO₃ and NiO-ZrO₂/WO₃ would be a solid superacid. Superacid properties are attributed to the inductive effect of W=O of tungsten oxide supported on ZrO₂ (13).

NiO-ZrO₂ alone without WO₃, whose acid strength was found to be $H_0 \leq -3.0$, was totally inactive for the dimerization reaction at room temperature. These results indicate that ethylene dimerization requires acid sites stronger

TABLE 1

Specific Surface Area of NiO-ZrO₂/WO₃ Catalysts Calcined at 700°C

Catalyst	Surface area (m ² /g)	Catalyst	Surface area (m ² /g)
2.5-NiO-ZrO ₂ /15-WO ₃	88	32-NiO-ZrO ₂ /15-WO ₃	86
14-NiO-ZrO ₂ /15-WO ₃	98	40-NiO-ZrO ₂ /15-WO ₃	76
20-NiO-ZrO ₂ /15-WO ₃	106	50-NiO-ZrO ₂ /15-WO ₃	72
25-NiO-ZrO ₂ /15-WO ₃	114		

TABLE 2

Acid Strength of Several Samples

Hammett indicator	pK _a value of indicator	NiO-ZrO ₂	ZrO ₂ /WO ₃	NiO-ZrO ₂ /WO ₃
Benzeneazodiphenylamine	+1.5	+	+	+
Dicinnamalacetone	-3.0	-	+	+
Benzalacetophenone	-5.6	-	+	+
Antraquinone	-8.2	-	+	+
Nitrobenzene	-12.4	-	+	+
2,4-Dinitrofluorobenzene	-14.5	-	+	+

than $H_0 = -3.0$. ZrO₂/WO₃ alone without nickel was also inactive for dimerization. Nickel oxide added with WO₃ exhibited a low activity for the dimerization, but nickel oxide without WO₃ was totally inactive. Therefore, the active site responsible for dimerization is suggested to consist of a low-valent nickel and an acid, as observed in the NiO-containing catalysts (7-10, 14). In fact, it is known that WO₃ supported on ZrO₂ or Al₂O₃ is an acid (13, 15). The term "low-valent nickel" originated from the fact that the NiO-SiO₂ catalyst was drastically poisoned by carbon monoxide, since a low-valent nickel is prone to chemisorb carbon monoxide (7). In this work, all catalysts added with WO₃ were poisoned by 1 μmol g⁻¹ of carbon monoxide for dimerization. It seems that the formation of low-valent nickel is caused by evacuation at high temperature followed by oxygen vacancy.

The existence of both Brønsted and Lewis acid sites was shown by the IR spectra of pyridine adsorbed on NiO-ZrO₂/WO₃ catalyst. X-ray powder diffraction showed that NiO-ZrO₂/WO₃ was amorphous up to 600°C of calcination temperature, but that the sample calcined at 700°C exhibited only tetragonal phase of ZrO₂.

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