pletion within one hour. Reactions were run under a nitrogen atmosphere and bath temperature were maintained at 25°C by using a cooling coil. Product isolation was straightforward.

The reaction mixture were filtered to remove catalyst and carbon. The filtrates were concentrated on a rotary evaporator. The residual solid was recrystallied in ethanol-pentane to give the corresponding hydrogenated product. The fractional distillation was done in case of liquid. The products were characterized by comparison of their physical and chemical properties with those of authentic samples.

The exclusive source of hydrogen, hydrazine was shown when *t*-stilbene was recovered quantitatively from a reaction mixture in which hydrazine was omitted. Using activated charcoal only or simply hydrazine and olefin gave no reaction with heating or sonication. The catalyst can be activated prior to the reaction by exposing it to sonic waves. However, the rates of hydrogenation were increased only by 5% when stirring. The short reaction times, mild condition, and complete hydrogenation observed in these sonic induced heterogeneous reaction may be from increased surface area of the catalyst caused by sonic fragmentation of the carbon support, or sonic activation of the palladium surface. We are presently investigating reduction of nitro group with metal-hydrazine and will report on them in due course.

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New Synthesis of Solid Catalyst for Ethylene Dimerization

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Ethylene dimerization is an important reaction and worthy of study.[1-4] We have synthesized a new catalyst which is very active for ethylene dimerization even at room temperature.

The catalyst was prepared as follws. The coprecipitate of $Ni(OH)_2$-$Ti(OH)_4$ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of nickel chloride, titanium tetrachloride, and hydrochloric acid at room temperature with stirring until the pH of mother liquid reached about 7. 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 (2g) was powdered below 100 mesh and was treated with 30m*l* of 1N H_2SO_4 followed by drying. It was used as catalyst after decomposing at different evacuation temperature for 1.5 h.

The catalytic activities for the reaction of ethylene dimerization were examined and the results are shown as a function of

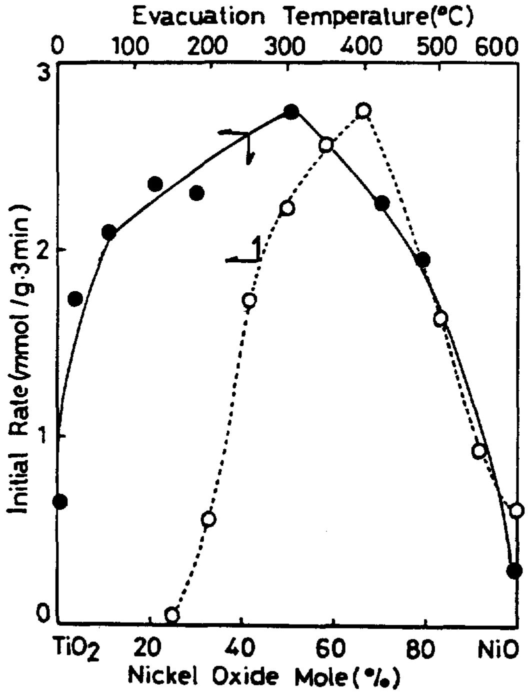

Figure 1.Variations of initial rate of ethylene dimerizaiton with composition of catalysts and evacuation temperature. ● evacuated at 400°C. O; equimolar mixture catalyst of nickel oxide and titanium oxide.

catalyst composition in the figure. The catalytic activity for ethylene dimerization was determined at 20°C by a conventional static system following pressure change from an initial pressure of 280 torr. Fresh catalyst sample of 0.2g was used for every run and the catalytic activity was calculated as the amount of ethylene consumed in the initial 3 mininutes. Reaction products were analyzed by gas chromatography with a VZ-7 column at room temperature.

Different mole ratios of nickel oxide-titanium oxide were tested for their activities. It can be seen that the maximum rate is obtained at around equimolar composition. An equimolar coprecipitate of nickel hyroxide and titanium hydroxide was decomposed at different evacuation temperature and tested for its activity. It can be seen that the activity appears above 200°C reaching a maximum at 400°C. On all the catalysts of NiO-TiO_2 treated with H_2SO_4, ethylene was selectively dimerized to n-butenes. In the composition of *n*-butenes analyzed by gas chromatography, 1-butene was found to predominate exculusively at the initial reaction time as compared with *cis*-butene and *trans*-butene. However, it was shown that the amount of 1-butene decrerases with the elapse of reaction time, while the amount of 2-butene increases with that of reaction time. It was also observed that the specific surface area attained a maximum by the equimolar mixture of nickel oxide and titanium oxide, and the evacuation at 400°C. On the other hand, a series coprecipitated samples as well as nickel oxide, and titanium oxide by themselves which were not treated with H_2SO_4 were nearly inactive as catalyst for ethylene dimerization. Nickel oxide treated with H_2SO_4 exhibited very low activity for ethylene dimerization, while titanium oxide treated with H_2SO_4 exhibited low activity for ethylene polymerization, as shown in the figure.

According to the IR spectra, the catalyst treated with H_2SO_4 possessed the bidentate sulphate ion coordinated to the metal.[5] The existence of both Brönsted and Lewis acid sites was shown by the IR spectra of pyridine adsorbed on the catalyst. In respect of crystalline structure, it was different depending on the evacuation temperature. They showed amorphous structure up to 400°C, rutile and nickel titanium oxide at 450°C, rutile, anatase and nickel titanium oxide at 500°C, and only anatase after the evacuation of 550°C.

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Development of Catalysts for the Synthesis of Some Intermediate Fine Chemicals. (I) An Efficient Method for the Di-C-Ethylation of Ethyl Acetoacetate. Alkylation of Crowded Carbanions*

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Factors governing the reactivity of bimolecular nucleophilic substitution (S_N2) reactions are well known. For example, dipolar aprotic solvents greatly enhances the reactivity of anionic nucleophiles toward neutral substrates.[1] Introduction of bulkier groups at the reaction center of the substrate retards the reaction. The reactivity of a nucleophile is greatly reduced when it becomes more crowded.

In this study, the ethylation of ethyl acetoacetate anion (EAA^-) with ethyl bromide is investigated. Various products obtained by the reaction are indicated in eq 1 and 2.

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