

Isomerization of 5-Vinyl-2-norbornene Using Sodium-coated Catalysts

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Various sodium-coated metal oxide catalysts were prepared using readily available supporting materials such as neutral γ -Al₂O₃ (neutral alumina, N-Al₂O₃) basic γ -Al₂O₃ (basic alumina, B-Al₂O₃), SiO₂, MgO, and TiO₂, and their catalytic activities were evaluated for the isomerization of 5-vinyl-2-norbornene (VNB) to 5-ethylidene-2-norbornene (ENB). Of various sodium-coated catalysts, Na/N-Al₂O₃ and Na/B-Al₂O₃ showed extremely high activities, resulting in quantitative conversion of VNB. Catalyst characterization and isomerization results clearly demonstrated that the presence of both strong basic sites ($\text{p}K_{\text{BH}} \geq 27$) and one-electron donor sites on the Na/Al₂O₃ is prerequisite for the isomerization of VNB to take place.

Key Words : Double bond isomerization, 5-Ethylidene-2-norbornene, EPDM rubber, Solid base catalyst

Introduction

5-Ethylidene-2-norbornene (ENB), a third component of a terpolymer of ethylene, propylene, and diene monomers (EPDM rubber), has been synthesized from the isomerization of 5-vinyl-2-norbornene (VNB), as depicted in Scheme 1.¹⁻³ As catalysts for the isomerization, there are known strongly basic homogeneous systems including NaH-polyamine, alkali metal alkoxide-aprotic solvent, or alkali metal amide-amines, but the industrial application of these catalytic systems has been restricted due to their low catalytic activities or to the difficulty in catalyst recovery.^{4,5}

There are also known solid super base catalysts such as alkali metal supported on alumina, silica gel, or active carbon with a large surface area, but these catalysts require extreme care in handling due to their instability toward air and water.⁶⁻⁹ Nonetheless, as long as the reaction can be conducted in an airless condition, heterogeneous catalyst system is more attractive than the homogeneous catalyst system in terms of industrial point of view because there is no need of solvent and catalyst recovery.

In general, doping of alkali-metal on a support is carried out by evaporating and condensing alkali metal vapor onto the support at elevated temperatures under high vacuum. Various metal oxides including MgO, CaO, BaO and TiO₂ have been employed as supporting materials,¹⁰⁻¹² but only Na-doped alumina was intensively studied as a catalyst for the isomerization of double bond.^{6-8,13}

Herein, we report on the preparation and characterization of various types of sodium-doped metal oxide catalysts as

well as their catalytic activities for the isomerization of VNB.

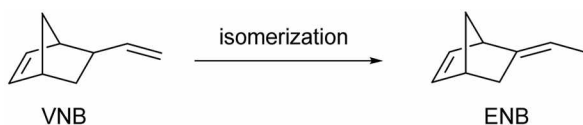
Experimental Section

Materials. VNB (TCI) was distilled from NaH under a reduced pressure and stored in glove box. Na metal, NaH, neutral γ -alumina, silica (fumed), magnesia (heavy) and titania (anatase) were purchased from Aldrich. Basic γ -alumina was prepared by treating neutral γ -alumina with excess amount of 10 wt% aqueous NaOH solution followed by filtration and drying at 120 °C for 3 h. All the glassware was flame-dried prior to use to remove water.

General procedure for the preparation of Na doped metal oxide catalyst. Na metal (1 g) and pre-dried γ -Al₂O₃ (9 g) at 500 °C for 5 h were charged into 250 mL round bottomed flask in an argon atmosphere and heated to 120 °C. As the solid mixture was stirred at 120 °C under vacuum (10⁻³ Torr), sodium metal started to melt and deposited onto the surface of alumina. After the completion of the Na coating, the resulting gray powder was aged at 120 °C for 2 h. The flask was then cooled down to room temperature and the prepared Na/N-Al₂O₃ was stored in a glove box. Other Na-supported catalysts including Na/B-Al₂O₃, Na/MgO, Na/SiO₂ and Na/TiO₂ were similarly prepared.

Isomerization of VNB. 10 g of VNB was added to a 100 mL flask containing 0.5 g of catalyst under the argon atmosphere, and reacted for 1 h at room temperature with vigorous stirring. The resulting solution was analyzed using GC (Agilent 6890, column HP 5, FID) and GC Mass (Agilent 6890 GC-5973 MSD).

Base strength distribution. The strength of basic sites on the prepared catalyst was determined using following indicators: 4-nitroaniline ($\text{p}K_{\text{BH}} = 18.4$), aniline ($\text{p}K_{\text{BH}} = 27$), and diphenyl methane ($\text{p}K_{\text{BH}} = 35$). Inside a glove box, a catalyst (0.2 g) in dry deoxygenated diethyl ether (5 mL)



Scheme 1. Isomerization of VNB to ENB.

containing an indicator was titrated with benzoic acid (8.28×10^{-2} M in ether). End point was detected by color change of the catalyst solution.

UV-Vis experiments. Inside the glove box, 2 mL of benzophenone solution in dry ether (0.04 M) was added to the 0.2 g catalyst in dry ether (2 mL). The color change to greenish blue indicates the presence of the phenyl ketyl radical. The UV absorption of the catalyst-benzophenone solution was measured using UV-Vis spectrometer (Sinco S-3100) under argon atmosphere.

Results and Discussion

The double bond migration of VNB to thermodynamically more stable ENB proceeds only in the presence of a strong base catalyst because the acidity of an allylic proton at the C-5 carbon of VNB is relatively low. Table 1 shows the result of isomerization of VNB using various solid base catalysts. Unsupported Na and NaH were completely inactive for the VNB isomerization even at high temperatures. CaO, prepared from CaCO₃ by treating 10^{-5} torr vacuum under 700 °C for 5 h, gave poor isomerization yield of 7%. However, when 10 wt% sodium-coated neutral γ -alumina, Na/N-Al₂O₃, was used as a catalyst, VNB was quantitatively transformed into ENB at room temperature in 1 h.

The isomerization activity of Na-coated catalysts was strongly dependent on the support employed. As can be seen in Table 2, Na-coated catalysts on SiO₂, MgO and TiO₂ were almost inert to the isomerization, whereas Na-coated catalysts on N-Al₂O₃ or B-Al₂O₃ convert VNB to ENB quantitatively at room temperature.

The isomerization of VNB is known to proceed through a carbanionic mechanism, in which the first step is the base-

mediated abstraction of C-5 proton and thus the base strength becomes an important factor in the catalysis.⁶ To correlate the activity of the prepared sodium coated catalysts with their base strengths, the distribution of base strength was measured using Hammett-Deyrup H-function. It is assumed that if a solid base can change the color of an indicator, the base strength of the solid is greater than or at least equal to the pK_{BH} of the indicator.¹⁴⁻¹⁶ Three kinds of indicators having different pK_{BH}, 4-nitroaniline (pK_{BH} = 18.4), aniline (pK_{BH} = 27) and diphenyl methane (pK_{BH} = 35), were used for the determination of base strength of Na-coated catalysts.

Table 3 reveals that the isomerization activity of the Na-treated catalyst is proportional to the basicity distribution and its concentration. All the catalysts were found to possess base sites with pK_{BH} value greater than or equal to 18.4, however, stronger base sites equal or higher than pK_{BH} = 27 was observed only in Na/N-Al₂O₃ and Na/B-Al₂O₃. Furthermore, in Na/B-Al₂O₃, 0.84 mmol/g of super basic site (pK_{BH} \geq 35) was also detected, which corresponds to 20% of added sodium. On the contrary, no color change was observed at Na coated MgO, SiO₂ and TiO₂ when they were treated with aniline or diphenyl methane solution. These results clearly indicate strong basic site with pK_{BH} greater than or equal to 27 play a decisive role for the isomerization of VNB.

In a previous paper, we reported that the isomerization of VNB, conducted in the presence of a homogeneous catalytic system composed of NaH-ethylene diamine, proceeds *via* a radical mechanism.⁵ As in the case of NaH-ethylene diamine system, the activity of Na/Al₂O₃ was also quenched completely when treated with 1,1,6,6-tetramethylpiperidinyl-oxide (TEMPO), suggesting that the active sites of Na/Al₂O₃ are strongly related to unpaired electron donor sites.

To measure the concentration of one electron donor sites, each Na-doped catalyst was treated with a benzophenone solution because the color of the solution changes to a characteristic greenish-blue color of the phenyl ketyl radical upon interaction with anionic one-electron species. Figure 1 shows that the intensity of the UV absorption peak of the resulting solution is the highest for Na/B-Al₂O₃. Na-coated on N-Al₂O₃, MgO, and TiO₂ gave absorption peaks with very low intensities, indicating that the concentrations of one-electron donor sites are quite low. The intensity of UV absorption peaks was also proportional to the activity of the catalyst as in the case of basic site distribution experiment.

From the basicity measurement and phenyl ketyl radical detection experiment, it could be concluded that both strong base sites (pK_{BH} > 26) and one-electron donor sites are required for the Na-coated catalyst to be active for the isomerization of VNB to ENB. N. Sun et al observed strong

Table 1. Activities of various solid base catalysts for the isomerization of VNB^a

Catalyst	Temp (°C)	Yield (%)
Na	25	n.r.
Na	120	n.r.
NaH	25	n.r.
CaO	25	7.1
Na/N-Al ₂ O ₃	25	99.9

^aReaction condition: VNB 10 g, catalyst: 0.5 g, rt, 1 h. ^bCaO was prepared by heating CaCO₃ at 700 °C under 10^{-5} Torr for 5 h.

Table 2. Activities of various Na-supported catalysts for the isomerization of VNB^a

Catalyst	Surface area of support (m ² /g)	Yield (%)
Na/N-Al ₂ O ₃	148	99.9 (76.8) ^b
Na/B-Al ₂ O ₃	164	99.9 (99.9) ^b
Na/MgO	14	n.r.
Na/SiO ₂	260	n.r.
Na/TiO ₂	19	n.r.

^aReaction condition: VNB 10 g, catalyst: 0.5 g, rt, 1 h. ^b20 g of VNB was used.

Table 3. Basic site distribution of Na-treated catalysts (mmol/g)

pK _{BH}	Na/N-Al ₂ O ₃	Na/B-Al ₂ O ₃	Na/MgO	Na/SiO ₂	Na/TiO ₂
>18.4	3.9	4.2	2.4	1.8	2.2
>27	3.5	3.9	-	-	-
>35	-	0.84	-	-	-

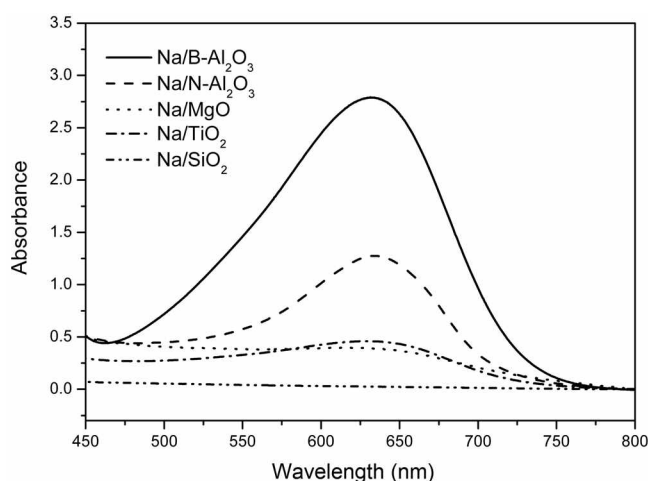


Figure 1. UV spectra of benzophenone solutions containing a Na-treated catalyst.

base sites and one-electron donor sites in the potassium-doped nanocrystalline MgO, where potassium cation and free electron were trapped into the edge/corner site on MgO.¹⁶ Likewise, in the Na-coated catalyst on Al₂O₃, Na is likely to be ionized to Na⁺ and free electron and trapped on the surface of alumina to make strong base sites and one electron donor sites. However, in the case of MgO and TiO₂, the concentration of edge/corner sites where free electron could be captured is very low because of their low surface area as shown in Table 2. As a result, formation of one-electron donor sites and strong base sites seems to be limited on the surface of the supports. In the case of SiO₂, although it has a high surface area, the ionization of Na is highly unlikely due to the high minus zeta potential of the silica surface as reported in the previous study.¹⁷

The higher concentration of strong base sites and one electron donor sites on NaOH treated alumina (B-Al₂O₃) can be rationalized by the absence of residual -OH group on the

neutral Al₂O₃ due to the reaction with NaOH, thereby preventing the consumption of the coated Na metal.

Conclusions

The isomerization of VNB was successfully carried out using Na-doped catalysts on neutral γ -Al₂O₃ and basic γ -Al₂O₃. The higher catalytic activities of these catalysts can be ascribed to the presence of both strong base sites ($pK_{BH} \geq 27$) and one-electron donor sites on their catalyst surfaces.

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