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Article

Dimerization of norbornene on zeolite catalysts



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ABSTRACT

The high activity and selectivity of H-Beta and H-ZSM-12 zeolites in the dimerization of norbornene was established. The norbornene conversion reached 100% in chlorinated paraffin and argon gas medium, with a selectivity of dimer formation of 88%–98%. Four stereo-isomers of the bis-2,2'-norbornylidene structure were identified in the dimer fraction, with the (Z)-anti-bis-2,2'-norbornylidene prevailing over the others.

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1. Introduction

The dimers of norbornene are used as a high density rocket propellant [1]. The norbornene dimer structure is a function of the nature of the catalyst and the reaction conditions. The photodimerization of norbornene in the presence of complexes of Cu(I) leading to the formation of cyclobutane compounds (Scheme 1) was first reported by Arnold et al. [2].

This reaction and the structure of the dimers formed under the influence of Ag(I), Tl(I), and Cu(II) triflates [3] were also studied by Trecker et al. [4] and Salomon. In the presence of $\text{NiCl}_2(\text{PPh}_3)_2$ and Zn powder in tetrahydrofuran, the reductive dimerization of norbornene resulted in the formation of the product **2** (Scheme 2) [5].

With other Ni-containing catalysts such as $\text{NiCl}_2\text{L}_2/\text{NaBH}_4/\text{ROH}$ (where $\text{L} = \text{PPh}_3, \text{PBu}_3, \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$) norbornene is dimerized to give compounds **3** and **4** (Scheme 3) [6,7].

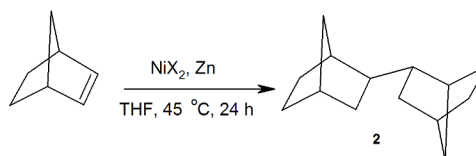
The formation of four bis-2,2'-norbornylidene (**5**) stereo-isomers has been detected in the products of metathesis polymerization of norbornene catalyzed by $\text{WCl}_3, \text{MoCl}_5$, and

ReCl_5 (Scheme 4) [1,8].

Compound **5** can be synthesized selectively enough with the catalytic complexes developed by a group of Polish scientists [9–13]. For example, the compounds in question (**5**) are formed on the binuclear carbonyl complex of $(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}$

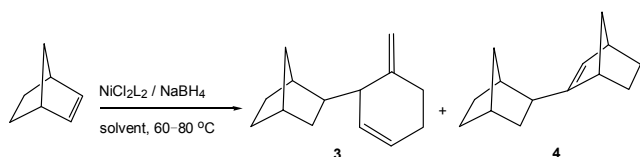


Scheme 1. Photodimerization of norbornene.



Scheme 2. Reductive dimerization of norbornene.

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Scheme 3. Dimerization of norbornene.

(SnCl_3)(CO) $_3$ with a yield of 68% [10].

Heterogeneous catalysts for the oligomerization of norbornene were less studied. Mobil Oil Corporation has patented two inventions related to the production of norbornene oligomers [14,15]. In the patent [14], the synthesis of the norbornene dimers of structure **1** was performed in the presence of reduced CrO_3 on a large pore silica gel. In patent [15] for the synthesis of the norbornene dimers of the structure **5**, they proposed the use of zeolites with the pore dimension of 0.5–0.8 nm of the ZSM family, MCM-22, PSH-3, SSZ025, and Beta zeolite. The norbornene conversion in the presence of ZSM-5 under atmospheric pressure and the boiling temperature of the olefin amounted to 80.7%. 95% of the reaction mixture contained dimers and trimers formed in the weight ratio of 3.8/1. It was demonstrated that the heat of combustion of the norbornene dimers **5** was close to the heat of combustion for rocket propellant JP-10, being 41.9 and 39.4 MJ/L, respectively [15].

However, the reported data did not explain the effect of the zeolite structure on the catalytic properties and whether the selectivity of the norbornene dimer formation can be altered by varying the reaction conditions.

This work reports on the structure effect of Y (FAU-type), Beta (BEA-type), ZSM-12 (MTW-type), and ZSM-5 (MFI-type) zeolites as well as the variation of the reaction conditions on the composition of the norbornene conversion products.

2. Experimental

2.1. Chemicals

For the synthesis, we used freshly distilled norbornene from Acros Company of 99% purity. The solvents, namely, nonane, chlorobenzene, methylene chloride, chloroform, carbon tetrachloride, tetrahydrofuran were purified prior to the runs by standard techniques [16].

2.2. Catalysts

The Y, Beta, ZSM-12, and ZSM-5 zeolites were studied in their H form. The HY zeolite with the exchange degree of Na^+ to H^+ ions of 96% was obtained by decationating of the NaY zeo-

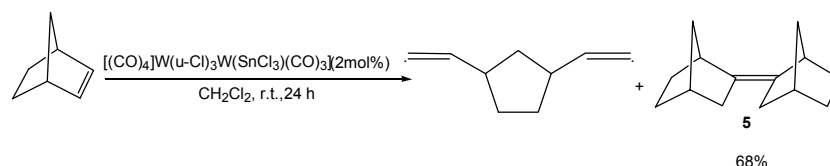
lite (the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 6.0) synthesized by the technique described in Ref. [17]. NH_4 -Beta ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 18.0$), H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 28.4$) and NH_4 -ZSM-12 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 34$) zeolites were manufactured by OJSC “Angarsk Plant of Catalysts and Organic Synthesis”. The NH_4 -Beta and NH_4 -ZSM-12 zeolite samples were converted into the H form by calcining at 540 °C. Prior to the catalytic runs, the zeolite samples were thermally treated at 540 °C in air for 4 h.

The catalysts were characterized by X-ray phase (XRP) and X-ray diffraction (XRD) studies, and temperature-programmed desorption of ammonia (NH_3 -TPD). For the equilibrium adsorption capacity of the samples by the vapor of water and benzene at 20 °C, the desiccator technique was used [18].

2.3. Dimerization of norbornene

A glass ampoule was loaded with the thoroughly dewatered solvent, norbornene, and freshly calcined catalyst in the amount of 10–30 wt% in Ar. The sealed ampoule was placed in the autoclave and rotated in a furnace controlled at 40–100 °C. After the suspension was cooled and the catalyst filtered off, the reaction mixture was obtained followed by the separation from it of four bis-2,2'-norbornylidene isomers by vacuum distillation. The conversion of norbornene and composition of the dimer fraction were determined by gas-liquid chromatography using a HRGS 5300 Mega Series «Carlo Erba» chromatograph with a flame ionization detector. The analysis conditions were: glass capillary column of 25 m length, SE-30 phase, temperature of analysis 50–280 °C, programmed heating of 8 °C/min, detector temperature of 250 °C, evaporator temperature of 300 °C, flow rate of helium carrier gas of 30 mL/min. The composition of the formed oligomers was analyzed by high performance liquid chromatography (HPLC) using a HP-1090 instrument. The analysis conditions were: Plgel 100Å polystyrene column, feed toluene flow rate of 0.8 mL/min, the ribbon speed of 1.5 cm^{-1} , refractive index detector.

The dimers of norbornene (**5a–5d**) were identified using GC-MS as well as uni- and bi-dimensional NMR spectroscopy. High resolution mass spectra were recorded using a Fisons Company instrument. Its chromatograph was equipped with a DB-560 capillary quartz column (50 m), the column was heated from 50 to 320 °C at 4 °C min^{-1} , the electron impact energy was 70 eV. ^1H and ^{13}C NMR spectra were recorded with a Bruker AVANCE-400 spectrometer with the working frequency of 400.13 MHz for the ^1H nuclei and 100.62 MHz for the ^{13}C nuclei using standard 5 mm diameter ampoules for solutions of substances in CDCl_3 . Benzene- d_6 and toluene- d_8 were used for the internal reference. 2D homo- (COSY HH) and hetero-nuclear (HSQC, HMBS) correlation experiments were performed using the pulse field gradient techniques.



Scheme 4. Metathesis polymerization of norbornene.

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