Characterization of ZHY and TCA/ZHY Catalysts for Hydration of α -Pinene

N. Wijayati, H. D. Pranowo, Jumina, Triyono, and G. K. Chuah

Abstract—The TCA/ZHY catalyst (Si/Al = 3.25) was prepared by impregnation of the Zeolite HY (Si/Al = 2.89) with amount of an aquous solution of TCA. The physico-chemical properties were investigated by XRD, ²⁹Si and ²⁷Al MAS NMR, BET, SEM, NH₃-TPD and FT-IR spectroscopy of pyridine adsorbed. The activity of catalytic of these catalysts has been carried out over the liquid-phase hydration of α -pinene to give α -terpineol as a major product and hydrocarbon as a minor products.

Index Terms—TCA/ZHY, a-pinene, a terpineol, hydration.

I. INTRODUCTION

H-Zeolites are natural or synthetic crystalline, microporous, aluminosilicate materials with with structures consisting of three dimensional frameworks of SiO₄ and AlO₄ tetrahedra linked through oxygen bridges [1]. Zeolite Y is a highly versatile molecular sieve from the faujasite family of zeolites whose 7.4 Å, three-dimensional pore structure and solid acidity make it useful as ion exchange, adsorption, heterogeneous catalysis, biosorption supports, polymer catalytic degradation and also attract interest in materials science for the development of functional materials and in nanotechnology [2]-[5]

Zeolite is used as molecular sieve. Species with kinetic diameter which make them too large to pass through a zeolite pores are effectively sieved [6]. Strong electrostatic field within a zeolite cavity results in a very strong interaction with polar molecules such as water. Furthermore, non polar molecules are also strongly absorbed due to the polarizing power of this electric field. Thus, excellent separations can be achieved by zeolites even when no steric hindrance occurs. Therefore, adsorption based on molecular sieve, electrostatic fields and polarity ability accounts for the considerable economic values of zeolite in adsorptive application [1]-[5].

The hydration reaction of α -pinene in the presence of zeolite catalysts has been well studied, and intensely so in the last ten years. Vital and co-workers [7] reported the use of solid acid catalysts such as zeolites and impregnated phosphomolybdic acid (HPMo) on polymeric membranes for

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 α -pinene hydration, achieving 100% conversion with selectivities for α -terpineol between 50% and 70%, although it required 150 h of reaction time. Mochida et al. [8] reported the use of zeolites and obtained 100% conversion, but with low selectivity for alcohols (around 57%). The TCA/ZrO₂ nH2O catalyst was active and selective for producing alcohols, with a conversion of 57% and a selectivity of 75% of total alcohols, and showed 57% selectivity for α -terpineol Avila et al. [9]

In this paper describes the characterization of the TCA/ZHY catalyst and the use in the hydration of α -pinene as catalysts for the formation of α -terpineol.

II. PROCEDURE

A. Experimetal

The catalysts were characterized by X-Ray Diffractometer (D-Max III (Rigaku) dengan radiasi Cu K α (α = 1.5378 A, 40kV, 30mA). The NMR spectra were obtained at 9.4 T on a Bruker DRX-400 spectrometer using 4mm ZrO2 rotors at room temperature. ²⁹Si MAS NMR spectra with high power proton decoupling were obtained at 79.49MHz with a spinning rate of 12 kHz, pulse length of 3 mikros and a recycle time of 20 s. 4 mm rotors were used and the ²⁹Si chemical shifts are repored relative to TMS. The ²⁷Al MAS NMR spectra were recorded at 104.26 MHz (9.4 T), with an excitation pulse of 1.7 mikros and a recycle delay of 5 s. The ²⁷Al chemical shifts were measured relative to aquous Al $(NO_3)_3$. The morphology and mean crystallite size of the zeolites were determined by scanning electron microscopy (SEM) in a JEOL JFC-1600 and JSM-6701F equipment. 1) Pt auto fine coater, Model: JEOL JFC-1600; Parameters: 20mA, 30sec coating time; Pt thickness: approx. 5nm. 2) FESEM. Model: JEOL JSM-6701F Voltage range: 0.1 -30kV, Magnification: 25X-650kX, Resolution: 1nm by specification. Physisorption of N₂, BET analysis was carried out on a Quantachrome® ASiQwin[™], Autosorb iQ Station adsorption analyzer. Prior to adsorption, the samples were outgassed at 300°C for 3 hours. NH₃-TPD experiments were carried out on a conventional setup equipped with a thermal conductivity detector. TPD profiles were obtained in a temperature range from 100°C to 500°C at a constant heating rate of 10°C /min in a 13 cm³ /min flow of helium. The IR spectroscopy of pyridine adsorbed (Py-IR) was carried out on a (Hitachi 270-50; Perkin Elmer Paragon 1000 PC; Shimadzhu FTIR-8201PC). GC-MS instrument (Agilent GC/MSD (7890A/5975C). The column used was DB-5MS 27m x 0.25mm x 0.25um B-5, Mass range: 41-500amu, Carrier gas flow rate: 1ml/min, Injector temperature: 260°C; Temperature program: 50°C (2min)-260°C(5min), heating

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rate 5°C/min; Flow: 1 mL/min; split ratio: 20. Note: 3uL of sample TP diluted with 1mL of methanol for GCMS analysis.

B. Catalitic Test

The reactions were carried out in a glass reactor equipped with magnetic stirrer, sampling port, temperature bath, and condenser. A mixture of 1.84 mmol of α -pinene, 2.5 mL of H₂O, and 3.4 mL of isopropyl alcohol was loaded into reactor. The mixture was stirred and warmed up to the desired temperature. Once the desired temperature was reached, the 400 mg of catalyst was added into the reactor. The reaction products were analyzed by GC by taking samples at 10, 20, 30, 60, 120, and 240 min after the addition of catalyst. The samples were taken at diferent interval of time to study the variation of reactant concentration and product. The samples were centrifuged at high speed of rotation (350 rpm) for about 10 min at ambient temperature to ensure that they were free of solid catalyst. Peak identification of the products were done by GC-MS analysis

III. RESULT AND DISCUSSION

A. XRD

The X-ray powder diffraction (XRD) patterns of the ZHY and TCA/ZHY with SiO_2/Al_2O_3 were shown in Fig. 1. The XRD patterns show that all the samples were zeolites topology, well crystallined and are free from impurities. Furthermore, the XRD patterns were used to calculate the average crystal size and the relative crystallinity of the different zeolites [1].

The relative crystallinity of the modified zeolites was calculated by comparing the average intensities of the most intense peaks with that of the parent zeolite, HY, assuming 100% of crystallinity for the starting material. The crystal size and relative crystallinity of the ZHY and TCA/ZHY.



Fig. 1. XRD patterns of ZHY and TCA/ZHY catalysts

B. 29Si MAS NMR

The ²⁹Si MAS NMR spectra of the ZHY and TCA/ZHY samples are shown in Fig. 2. It is well known that a ²⁹Si MAS NMR spectrum of the ZHY may contain up to five lines depending on the number of aluminum atoms and silanol groups connected to the silicon atom. The ²⁹Si MAS NMR

spectrum of the parent ZHY sample shows the presence of four components, corresponding to Si(0Al), Si(1Al), Si(2Al) and Si(3Al) species at -108, -102, -99, and -94 ppm, respectively, similar to that observed by Yan et al, [10]



Fig. 2. ²⁹Si MAS NMR spectra of ZHY and TCA/ZHY

After impregnated by 35% tricholoacetic acid under reflux for 5 h, the intensities of these lines are nearly unchanged, which suggests that the framework structure is kept almost intact. However, with the concentration of the TCA solution, there is another line developed at -112 ppm, which is assigned to Si(4Si) of silica. At this stage, some of the framework Al species are removed from the lattice by TCA and a large part of the framework is ruined, as indicated by its corresponding XRD pattern (Fig. 1). Meanwhile, it is clear that other bands (those at -108 and -103 ppm) become broadened as compared with the parent ZHY, suggesting that impregnated TCA leads to a distortion of the coordination environment of the corresponding framework silicon atoms and, thus increases the chemical shift distribution. It is necessary to make an unambiguous assignment of the peaks at -94 and -102 ppm because, for example, in the case of ZHY, we can hardly attribute them solely to the Si(3Al) and Si(1Al) species, respectively. As can be seen, compared with Fig. 2, the relative ratio of the intensity of the line at -102ppm to that at -108 ppm increased in the spectrum of the TCA/ZHY, suggesting that the line at -102 ppm may be partly due to the (OSi)₃SiOH species that contains a silanol group. Thus, the line at -102 ppm is in fact an overlap of Si (1Al) and (OSi)₃SiOH sites in the spectrum of parent ZHY. After the impregnated by the 35% TCA, the intensity of the line at -102 ppm is further increased with respect to that of the line at -108 ppm, and attains the maximum. This fact shows that TCA can remove lattice aluminum from the zeolite framework, thus resulting in the so-called silanol nests, which is confirmed by the following ²⁷Al MAS NMR spectra which show an increase in the intensity of the silanol groups at 1.7 ppm. The enhanced signals at -93 ppm illustrate the presence of the (SiO)₂ Si(OH)₂, also due to Al removal. Moreover, the peak at -112 ppm corresponding to Si(4Si) of silica becomes more obvious.

C. 27Al MAS NMR

The ²⁷Al MAS NMR has been widely used to follow the local Al environment as a function of the treatment. ²⁷Al MAS NMR spectra of ZHY show two components were detected centered at 0 and 60 ppm, corresponding to octahedrally and tetrahedrally-coordinated Al species, respectively, can be clearly distinguished [10]-[12]. At the

same time, for the TCA/ZHY samples, the peaks at around 60 and 0 ppm undergo different changes. As shown in Fig. 3, both the peaks at 60 and 0 ppm seem to become narrowed upon a TCA/ZHY. It is especially the case for the one at 0 ppm. Here, with impregnated 35% TCA, resulting in the narrowing of the band at 0 ppm and the intensity of the 60 ppm peak decreases. ²⁷Al MAS NMR signals at ca. 60 ppm (Al^{IV}) and the signals at ca. 0 ppm are due to octahedrally coordinated aluminum species (Al^{VI}) [13].



Fig. 3. ²⁷Al MAS NMR spectra of ZHY and TCA/ZHY

D. SEM

Scanning electron microscopy (SEM) concludes that the morphology of the outer surface of the zeolite crystals is vitually not affected by TCA treatment (Fig. 4).



Fig. 4. SEM image of ZHY and TCA/ZHY in different magnifications

E. BET (N2 Adsorption-Desorpsi)

Table II shows the textural properties of the ZHY and TCA/ZHY catalysts. The BET surfaces of the TCA/ZHY catalyst was lower than those of the ZHY, with an observed decrease of 13.54%. The pore diameter (Dp) volumes of the TCA/ZHY catalyst was also lower than ZHY, decreased (29.43%) with respect to that of the ZHY. In the case, the pore volume of TCA/ZHY was higher than ZHY, with an observed increase of 12.12%. This increase is difficult to justify, and this small difference can be attributed to the low precision of the BJH method in the micropore region. The adsorption isotherms for the ZHY and TCA/ZHY are of type IV according to IUPAC classification. The average pore

diameters of ZHY was slightly larger than 2 nm, the upper limit established by the IUPAC for mesopores (2-50 nm) [13]. In this type of isotherm for TCA/ZHY, the adsorption takes place at relatively low pressures and was characteristic of microporous solids, the average pore diameter was lower than 2 nm.

TABLE II: TEXTURAL PROPERTIES OF THE CATALYSTS DETERMINED OF BET



Fig. 5. $N_{\rm 2}$ adsorption–desorption isotherms at 77 K for ZHY and TCA/ZHY

This is indicated that samples of ZHY have larger surface area and pore volume than the TCA/ZHY, due to the larger number of tetrahedral silicon and aluminum species in zeolite skeleton in the former and the more complete pore structure formed.

F. Acidity

The acidity of the ZHY and TCA/ZHY catalysts were characterized by the NH₃-TPD and Py-IR. Temperatureprogrammed desorption (TPD) of ammonia often has been used to characterize the acidity of zeolites. First, desorbed ammonia peaks must be identified, because low-temperature desorption contains considerable amounts of ammonia physically adsorbed on NH_4^+ cations. Therefore, counting a low-temperature peak as an acid site mistakenly leads to overestimation of the number of acid sites. When the TPD is measured under normal conditions, it is controlled by the free readsorption does not simply correlate with the strength of acid sites [14].

 NH_3 -TPD was carried out to compare the acid strength and amount of the samples (Table III), and all samples had two NH_3 desorption peaks, which indicated that weak and strong acid sites were present in these samples (Fig. 6). For the TCA/ZHY catalyst, the amount of total acid sites decreased, and the strength of strong acid sites increased with the increasing of SiO₂/Al₂O₃ ratio.

The amount of Br önsted and Lewis acid sites of the studied samples, as determined by pyridine adsorption (FT-IR), are shown in Fig. 7. Py-IR spectra of two characteristic absorption peaks, of which 1543 cm⁻¹ and 1442 cm⁻¹, attributable to pyridine adsorbed on Br önsted acid and Lewis acid sites, respectively [15]-[17].

The amount of Brönsted acid sites provided by hydroxyl bridge skeleton decreased with the increasing of the SiO_2/Al_2O_3 ratio. Compared to TCA/ZHY pattern, the ZHY samples provided more Brönsted acid sites, which indicates more aluminum species enter into the framework. However, this results in accordance with the changes of strong acid sites detected by NH₃-TPD. It is thus clear that impregnation TCA to the ZHY can not only change the amount of acid sites, but also effectively change the distribution of acid sites.



Fig. 6. NH3-TPD ZHY and TCA/ZHY catalysts



Fig. 7. FT-IR spectra of ZHY and TCA/ZHY

G. Catalytic Acivity

Catalytic study were performed using ZHY and TCA/ZHY. The molecular size of α -pinene was estimated to be 0.62 × 0.59 × 0.53 nm, which is smaller than ZHY and TCA/ZHY catalysts [8]. The reaction was carried out in an excess of water with α -pinene as the limiting reagent. α -Pinene was almost immiscible in water at the reaction conditions. It forms a separated organic phase in the reactor. The reaction taken place over the catalyst surrounded by the aqueous phase. α -Pinene should adsorb on acid site to promote the acid catalyzed reaction the presence of water. The reaction product, i.e. α -terpineol, was non polar compounds and was extracted out into the organic phase simultaneously during of the reaction thereby giving significant conversion.

Effect of reaction time on the α -pinene conversion and selectivity of terpineol for ZHY and TCA/ZHY catalysts were shown in Fig. 8.



Fig. 8. Conversion and selectivity of α -terpineol vs. reaction time. Reaction conditions: 1.84mmol α -pinene, 2.5mL H₂0, 3.4mL (CH₃)₂CHOH, 400 mg catalyst, temperature 65°C; S= Selectivity; C= Conversion

To achieve a well mixing between the reagents and the α -pinene during reaction, they must be stirred well at constant rate. The observed conversion of α -pinene with TCA/ZHY was 1.43 times higher with respect to that observed with ZHY at from 10 min until 30 min, after that, the convertion with TCA/ZHY the same as ZHY until 120 min. The hydration reaction with TCA/ZHY, the highest selectivity of α -terpineol was 57.14% with a conversion of 73.80% at 20 min, whereas the higher conversion was 99.63% with selectivity of 30.79% at 120 min.

Fig. 4 show that the main products were α -terpineol, camphene, terpinolene, and limonene. Castanheiro, *et al.* [18] proposed reaction scheme for the acid catalyzed hydration of α -and β -pinene. They used molybdophosphoric acid as catalyst and obtained limonene, γ -terpinolene, and α -terpineol as main products.

The acid catalyzed the hydration reaction of alkenes in aqueous solution. The acid transfers a proton to double bond of the alkene forming an intermediate of carbocation. The carbocation can lose a proton and generate monocyclic and bicyclic hydrocarbons or, in the presence of a nucleophile, give to monocyclic alcohol. In the hydration of terpenes, variation products might be obtained depending on the catalyst and reaction conditions [8]-[9], [19], [20]

The catalyst of TCA/ZHY was studied for this hydration reaction. The internal surface of catalysts being highly hydrophobic possesses affinity towards non polar molecules like that of α -pinene [7]-[9]. Y-Zeolite showed high activity for α -pinene hydration, indicating the high potential of this catalyst as an alternative solid acid catalyst to conventional homogeneous catalyst. By Evaluating this work, was a good candidate for the industrial hydration of α -pinene, due to its easy separation from reaction products and low cost.

IV. CONCLUSION

XRD and SEM shows that the TCA/ZHY nanocrystals obtained are highly crystalline, and its pore volume is moderate Fig and its pore diameter 18.09 Å prove that it is a nanoporous material. ²⁹SiMAS NMR shows that TCA can remove lattice aluminum from the zeolite framework, thus resulting in the so-called silanol nests, which is confirmed by the following ²⁷Al MAS NMR spectra. The Si/Al ratio of ZHY and TCA/ZHY were 2.89 and 3.25, repectively. The TCA/ZHY nanocrystals show high N₂ adsorption; and BET

surface area and pore volume are determined to be 530 m2 g^{-1} and 0.099 cm3 g⁻¹ respectively. NH₃-TPD spectra show that impregnation TCA to the ZHY can not only change the amount of acid sites, but also effectively change the distribution of acid sites.

The TCA/ZHY was a good candidate for the industrial hydration of α -pinene, due to its easy separation from reaction products and low cost. The hydration of α -pinene catalyzed by TCA/ZHY was fast and leads mainly to monocyclic terpenes and alcohols with α -terpineol as the principal product (up to 57%).

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