Catalysis Letters Vol. 110, Nos. 1–2, August 2006 (© 2006)
DOI: 10.1007/s10562-006-0092-0

Dimerization of isobutene over nickel modified zeolites to obtain isooctene

Medina González Yaocíhuatl,[a,b] Hernández Luna Martín,[a] and Alcaraz Cienfuegos Jorge[a,*]

[a]*Departamento de Ingeniería Química, Laboratorio de Investigación de Procesos, Universidad Nacional Autónoma de México, Conjunto E, L-223 Facultad de Química, Circuito Institutos Ciudad Universitaria, Mexico DF, C. P. 04510, Mexico*
[b]*Laboratoire de Chimie Agroindustrielle, UMR 1010 INRA/INP-ENSIACET, Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques, 118 route de Narbonne, F-31077 Toulouse Cedex, France*

Received 22 February 2006; accepted 11 April 2006

Ni/H Zeolites catalysts were prepared by impregnation, starting from HY-Zeolite, Hβ-Zeolite and H-mordenite with nickel precursor salts, $NiCl_2$, $NiSO_4$ and $NiCO_3$. The total number, NTSA, and the acid strength were found dependent on the nickel precursor salt. High catalytic activity, selectivity and stability of the modified zeolites in isobutene dimerization was attributed to the acidic properties of nickel modified zeolites. HY-Zeolite modified with $NiCO_3$ resulted more active and selective to dimerization reaction. The prepared catalysts were characterized by EDSX, SEM, and Adsorption/Desorption of N_2 at 77 K, NH_3 chemisorption and Ammonia Temperature-Programmed-Desorption (NH_3-TPD) and FT-IR of adsorbed pyridine. NH_3-TPD and isobutene adsorption revealed an acid sites a new distribution and apparition of acid sites not present in the protonated zeolites. Catalytic activity and reactor behavior were studied in a continuous downstream fixed bed reactor at 298 K, 27.6 kPa (4 psig), and WHSV = 0.27 h^{-1}.

KEY WORDS: isobutene dimerization; nickel modified zeolites; olefin oligomerization.

1. Introduction

The clean air regulation in all countries concerning the contents of olefins, sulfur and aromatics, particularly benzene in gasoline will become increasingly strict. In addition, the removal of MTBE from gasolines in the US because of its negative environmental impact in ground water will further increase the need for high octane blending compounds in the gasoline pool. Hence, the diisobutenes can also be used as a feedstock to produce other high-octane components like isooctane or ethers like 2-methoxy-2,4,4- trimethyl-pentane and 2-ethoxy-2,4,4-trimethylpentane.

Solid acid catalysts for dimerization and oligomerization of olefins have been known for many years [1–3], especially catalytic systems consisting mainly of nickel compounds supported on oxides, zeolites and organometallic nickel complexes have been used as dimerization catalysts and several processes have been commercialized [4,5] using these catalysts to obtain low molecular weight branched products from olefins dimerization, because they are suitable as gasoline blending components.

Dimerization technologies available today were developed in anticipation of an impeding ban or phase-out of the oxygenate MTBE. These processes purport to dimerize butenes to isooctene and offer an optional step to hydrogenate the isooctene to isooctane, RON and MON blending values of 95–109 and 90–96, respectively.

Several technologies are available for commercialization, for example, Isoether process developed by Snamprogetti, to produce isooctane and CDIsoether technology by CDTECH, in these, isobutene can be dimerized to isooctane or partially dimerized and partially etherified.

In alkylation process developed by UOP using solid phosphoric acid, water is added to control the activity and selectivity of the operation.

In reality, current dimerization technologies produce not only isobutene dimers, but also trimers, tetramers, light ends and heavy ends. Despite, recent dimerization technologies has attracted the attention as an alternative to MTBE production.

This study focuses on the activity and selectivity of nickel modified protonated zeolites in the isobutene dimerization under mild conditions. Though all these zeolites have been studied before, they have not been compared under identical operating conditions. This paper investigates the effect of nickel precursor salt, the role of the acidity and the zeolites structures, including HY-Zeolite, Hβ-Zeolite and H-mordenite.

---

*To whom correspondence should be addressed.

1011-372X/06/0800–0107/0

2. Experimental

2.1. Catalyst preparation

Protonated zeolites (HY-Zeolite SiO_2/Al_2O_3 = 5.2, Hβ-Zeolite SiO_2/Al_2O_3 = 150 and H-Mordenite SiO_2/Al_2O_3 = 90) from Zeolyst International were immersed in different solutions of nickel precursor salts: nickel chloride, nickel sulfate and nickel carbonate supplied by Mallinckrodt, after filtered, the solid was dried for 12 h at 373 K and calcined for 5 h at 773 K to obtain modified zeolites.

Variation of nickel load over the catalyst was performed by changing the concentration of the nickel precursor salt solution in order to get a range of nickel content from 0 to 16.5 wt.%.

Table 2

SiO_2/Al_2O_3 ratio and its influence on catalysts total acidity

Catalyst	SiO_2/Al_2O_3 ratio	Acidity (mmol/g)
HβZ	150	0.37
HM	90	0.82
HYZ	5.2	0.82
B3	162.97	0.46
B5	99.33	1.3
B6	5.88	1.19
B7	5.94	0.8
B8	5.96	1.05

B6 HY-Zeolite modified with $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_20$, nickel load 3.2 wt%.

B7 HY-Zeolite modified with $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_20$, nickel load 6.2 wt%.

2.2. Catalyst characterization

Nitrogen adsorption/desorption at 77 K was performed to determine BET area, pore size distribution, pore total volume and average pore diameter.

For measuring the total acidity (NTSA), two different kinds of experiments were carried out: selective ammonia chemisorption at 313 K in a Quantachrome 1C system (results showed on tables 1 and 2) and Ammonia Temperature-Programmed-Desorption (NH_3-TPD) measured in flow system with a thermal conductivity detector (TCD). For TPD experiments, the sample of 200 mg was outgassed in helium flow at 673 K for 90 min which followed sample ammonia saturation by flowing 4.0% mol NH_3/He steam at 298 K for 30 min, after equilibration in He flow for 60 min at room temperature, the catalyst was heated in a linear rate of 10 K/min to 823 K and the detector signal of ammonia desorption was recorded. TCD response was calibrated by doses containing known amounts of ammonia. Data were collected and processed by computer software. NH_3-TPD was used to determine the acid strength for the modified zeolites (Figures 3 and 4).

The modified zeolites were characterized by Energy-Dispersive X-Ray Spectroscopy (EDSX) by using a JEOL5900LV equipment to determine nickel concentration and SiO_2/Al_2O_3 ratios (table 2).

2.3. Catalytic evaluation

The catalyst was crushed and sieved to a variety of particle size with average diameter ranging from 0.105 to 2 mm.

Before the initiation of the reaction in liquid phase, the catalysts were dried and sealed in a fragile glass cell containing 2 g of modified zeolite catalyst protected

Table 1

Catalysts prepared by impregnation of nickel from three different precursor salts over three different zeolites

Catalyst	Precursor salt/sopport	Solution molarity	Specific area (m^2/g)	Total pore volume (cc/g)	Average pore diameter (Å)
A1	$NiCl_2 \cdot 6H_20$/HYZ	0.17	n.m.	n.m.	n.m.
B2	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_20$/HYZ	0.06	556.4	0.4085	36.12
A2	$NiCl_2 \cdot 6H_20$/HYZ	0.013	519.1	0.2097	36.34
C1	$NiSO_4 \cdot 6H_20$/HYZ	0.13	404.4	0.124	36
A3	$NiCl_2 \cdot 6H_20$/HβZ	0.18	n.m.	n.m.	n.m.
B3	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_20$/HβZ	0.0106	468.9	1.005	88.31
A4	$NiCl_2 \cdot 6H_20$/HβZ	0.0067	n.m.	n.m.	n.m.
C2	$NiSO_4 \cdot 6H_20$/HβZ	0.0213	437.5	0.94	89.7
A5	$NiCl_2 \cdot 6H_20$/HM	0.051	197	0.0057	36
B4	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_20$/HM in acetic acid	0.0160	225.5	0.0064	45
A6	$NiCl_2 \cdot 6H_20$/HM	0.013	382.3	0.003	35.6
B5	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_20$/HM	0.013	394.7	0.178	35.9
C3	$NiSO_4 \cdot 6H_20$/HM	0.038	394.1	0.179	35.9
HYZ	–	–	660	0.1654	36.08
HβZ	–	–	650	0.886	87.54
HM	–	–	500	0.0086	36.2

HYZ catalysts with HY-Zeolite as support.

HβZ catalysts with Hβ-Zeolite as support.

HM catalysts with H-Mordenite as support.

n.m. not measured.

from contact with air, were introduced into the reactor, (Parr brand, 300 mL equipped with a temperature control, magnetic stirrer and a heating jacket), connected to vacuum line to evacuate the air inside the reactor. A dry ice bath was used to cool the reactor to about 0 °C in order to charge isobutene (Praxair 99.5 %); when the appropriate experimental conditions were reached 298 K, 965 kPa, (140 psig), isobutene weight = 70 g and stirrer velocity = 650 rpm), the glass cell was broken and the zeolite catalyst was dispersed in the liquid phase. This was the zero time. Several samples were taken in chilled flasks; identification of reagent and products were performed using a GC-FID (gas chromatography equipped with a flame ionization detector), using an HP-5 capillary column 30 m × 0.25 μm, injecting 0.1 μl of sample using a chilled syringe to minimize lost of volatile compounds that could be presents in the reaction mixture.

Isobutene conversion and isooctenes selectivity were calculated as showed in equations (1) and (2) were taken as the parameters to evaluate the performance of the tested catalysts in liquid phase.

$$\text{Conversion}_{\text{-isobutene}} = \frac{i - C_4^{\text{in}} - i - C_4^{\text{out}}}{i - C_4^{\text{in}}} \tag{1}$$

$$\text{Selectivity} = \frac{\text{yield of}(i - C_s)_n\text{products}}{i - C_4\,\text{conversion}} \tag{2}$$

$$i - C_4 = \text{isobutene}.$$

Gas phase reactions were performed using a fix bed reactor, (In-Situ Research Instruments), equipped with mass flow meters, a mixture of isobutene (2.0% mol) in nitrogen from Praxair was fed downstream; reactant and products were analyzed on line using a Hewlett-Packard 6890 FID gas phase chromatograph, equipped with an HP-5 5% crosslinked PH ME Siloxane column, 30 m × 0.25 μm injections were performed using an automatic valve.

The activity trials were used to obtain the best combination of support and precursor salt among those that were tested, HY-zeolite modified using $NiCO_3$ as precursor salt, showed the best performance in selectivity, activity and stability, therefore we decided to carry out this reaction in gas phase to study the effect that a change in nickel load, temperature, pressure, WHSV, feed flow and particle size had over isobutene activity and isooctenes selectivity. Gas phase was chosen to reduce diffusion effects.

3. Results and discussion

3.1. Influence of nickel precursors salts on catalyst properties

Details about the catalysts employed are summarized in Table 1.

Specific area showed a decrement with modification, mordenite showed the biggest decrement; this can be the result of a deterioration of the zeolitic framework structure due to calcination or framework dealumination evidenced by EDSX (tables 1 and 2).

The acidity characterizations of Bn catalyst series, irreversible NH_3 adsorption and NH_3 thermodesorption, indicated that it possessed a higher concentration of strong acid sites than protonated zeolite, HYZ (Figure 3). So, the total acidity and strength of acid sites distribution change and their influence on the catalyst performance were attributed to SiO_2/Al_2O_3 ratio and the nickel load.

3.2. Influence of operation pressure over catalytic activity

Pressure was another key parameter, an increase on this variable provoked condensation of isobutene over catalyst which can be beneficial to conversion, but can result on selectivity decrease due to interface diffusion problems so products continue oligomerizating inside the catalyst pores giving low selectivity. Nevertheless, at 90 psig of pressure, conversion of 0.9 was obtained over 70 h of reaction, after this time, conversion decreased to 0.75 and was maintained until 100 h of operation were reached (Figure 1).

3.3. Influence of reaction temperature over catalytic activity

An increase in this variable resulted in selectivity decrease as it was predicted by thermodynamics [5–7]; so it was decided to perform this reaction at room temperature (Figure 2).

3.4. Influence of acidity over catalytic activity

It should be noted HYZ would contain only acid sites, while B6-B8 catalysts series contain acid sites and nickel.

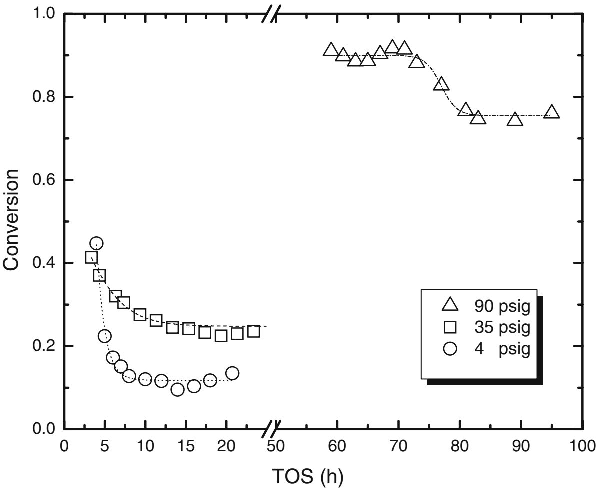

Figure 1. Influence of operation pressure over catalytic activity. T = 25 °C, WHSV = 0.09 h^{-1}, isobutene flow = 9.6 mL/h, B6 catalyst.

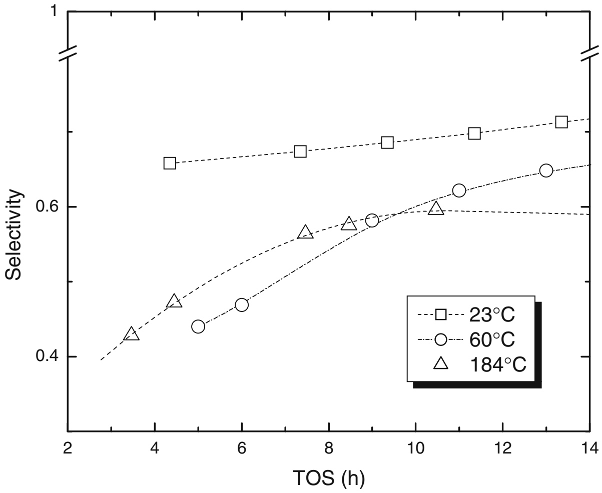

Figure 2. Influence of reaction temperature over selectivity to dimers of isobutene. P = 15 psig, WHSV = 0.09 h^{-1}, isobutene flow =9.6 mL/h, B6 catalyst.

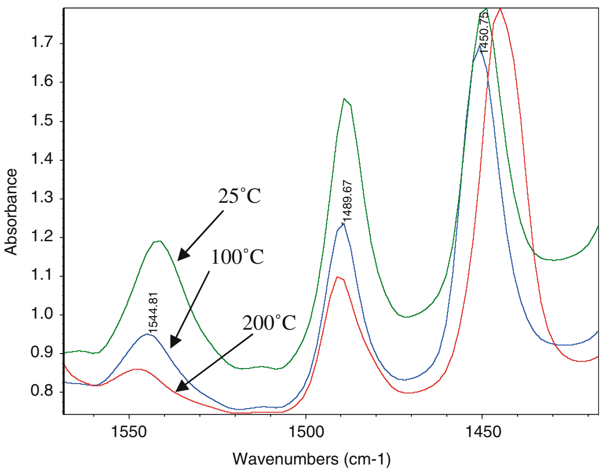

Figure 4. Pyridine adsorbed FT-IR spectra of B6 catalyst, adsorption temperature, 25, 100 and 200 °C.

The acidity characterization NH_3-TPD of B6 and HYZ catalysts was carried out to examine the relative strength of binding of the ammonia with the nickel and acid sites. Recent studies performed by Lemos *et al.* [8] has shown that NH_3-TPD thermogram could be linked to number and strength of acid sites. In the case of B6-B9catalysts, due to the substitution of $2H^+$ by Ni^{+2} we have obtained a decrement of weak sites, nevertheless, the number of strong acid sites augmented (Figure 3).

The catalysts desorbed a maximum ammonium quantity between 353 and 923 K for B2 catalyst, these desorption temperatures indicated that catalysts owns a high concentration of strong acid sites compared to protonated zeolite without nickel modification HYZ, which desorbed ammonia in the range of 353–773 K, (Table 3), however high selectivity to cracking products was no observed in the dimerization reaction.

The enhanced acidity and acid strength of this catalysts can be the result of a synergy between protons from support and Ni, like a specie H^+...Ni which suffers insertion of the olefin that is the beginning of the oligomerization mechanism, this increase of acidity can be due to the existence of free coordination sites on nickel, this sites allow olefins insertion and act as adsorption sites [9,10].

Infrared spectroscopic studies of pyridine adsorbed on catalysts prepared, have made possible to distinguish Bronsted, (1544 cm^{-1}) and Lewis sites, (1450 cm^{-1}) estimating the concentration and their relative acid strength, revealing a considerably higher relative concentration of strong acid sites in nickel modified catalysts, B6 (Figure 4 and table 4).

It has been claimed that the presence of strong Lewis sites acid sites promoted the formation of unsaturated compounds. The favored production of unsaturated carbenium ions with increased Lewis acidity was evidenced by Flego *et al.* [11].

Lewis acid sites adsorb isobutene and olefin concentration increases near the Bronsted acid sites. This increment in concentration enhances the probability of isobutene to be dimerized [12]. Thus, it is not only important to have a high number of Bronsted acid sites, but also at the same time as much as possible Lewis acid sites.

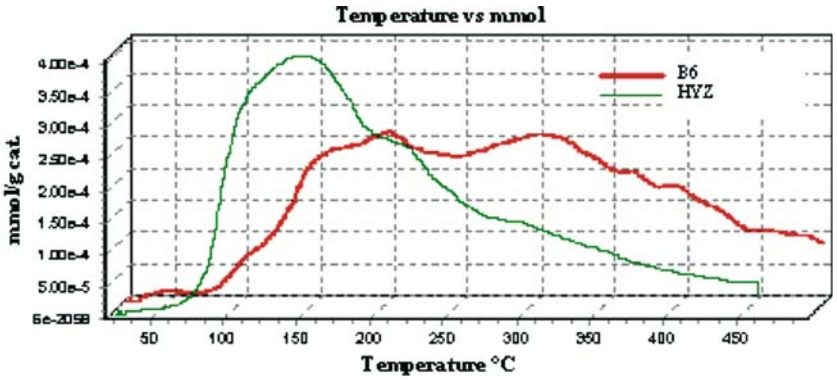

Figure 3. NH_3-TPD comparison of protonated zeolite HYZ and B6 catalyst.

Table 3
HYZ and B2 catalysts acidity strength comparison

Temperature range (K)	Catalyst HYZ (mmol/g cat)	Catalyst B2 (mmol/g cat)
353–473	0.4399	0.2294
473–673	0.3983	0.5663
Higher than 673	0.0479	0.2807
NTSA by NH_3 TPD	0.8861	1.0764
NTSA by NH_3 chemisorption	0.82	0.83

Table 4
Number and strength bronsted and Lewis acid sites by FT-IR spectra of adsorbed pyridine

Adsorption temperature (K)	Bronsted acid sites number (mmol/g cat)	Lewis acid sites number (mmol/g cat)	Acid sites total number (mmol/g cat)
293	0.068	0.923	0.991
373	0.098	0.411	0.509
473	0.097	0.206	0.303
573	0.061	0.125	0.186
673	0.026	0.086	0.112
773	0.0	0.0	0.0

3.5. Catalytic activity

After the analysis of precedent information and the isobutene conversion for the several catalysts prepared, it seemed appropriate to investigate the dimerization of isobutene over catalysts that associate the properties of HY-Zeolite and nickel carbonate.

Preliminary experiments were carried out to establish the optimum reaction conditions. At room temperature, 25 °C, activities of isobutene dimerization and oligomerization were measured in the kinetic regime. The reaction rates were not affected by external mass transfer, e.g., the yield of isooctene did not change upon a variation of the gas velocity, while the space time was kept constant by varying the volume of the catalyst simultaneously (Figure 5).

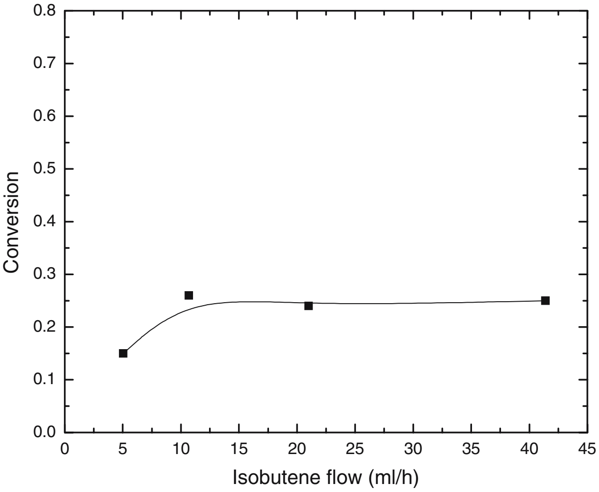

Figure 5. Conversion as a function of isobutene flow at WHSV = 0.09 h^{-1}, T = 25 °C, P = 4 psig.

Conversion and selectivity obtained in gas phase reactions are reported in table 5, it was observed that catalysts B6–B9 were more stable when used in dimerization reaction than protonated zeolite. Catalysts B6–B9 showed the highest conversion and selectivity to

Table 5
Temperature, pressure, WHSW, i-C_4 flow, particle size and nickel load variation using B6–B9 catalysts series in isobutene dimerization reaction

T (K)	P (psig)	WHSV, h^{-1}	i-C_4 flow (mL/h)	Particle size (mm)	Nickel load (%)	Selectivity	Conversion
298	5	0.09	11.3	0.3	0	0.75	0.24
298	5	0.09	11.3	0.3	3.2	0.87	0.28
298	5	0.09	11.3	0.3	6.2	0.86	0.13
298	5	0.09	11.3	0.3	9	0.77	0.23
298	5	0.09	11.3	0.3	16.5	0.75	0.15
298	4	0.09	11	0.3	9	0.85	0.23
298	4	0.09	11	0.7	9	0.85	0.2
298	4	0.09	11	0.9	9	0.75	0.14
298	4	0.09	11	2	9	0.85	0.14
298	4	0.05	11	0.3	9	0.8	0.12
298	4	0.07	11	0.3	9	0.72	0.18
298	4	0.09	11	0.3	9	0.75	0.19
298	4	0.14	11	0.3	9	0.98	0.08
298	4	0.27	11	0.3	9	0.98	0.026
298	4	0.09	5	0.3	9	0.72	0.15
298	4	0.09	10.7	0.3	9	0.74	0.26
298	4	0.09	21	0.3	9	0.75	0.25
298	4	0.09	11.3	0.3	9	0.75	0.25
298	4	0.09	12	0.3	9	0.78	0.23
298	35	0.09	12	0.3	9	0.8	0.12
298	90	0.09	12	0.3	9	0.27	0.7
296	15	0.09	9.6	0.3	9	0.7	0.24
333	15	0.09	9.6	0.3	9	0.61	0.26
457	15	0.09	9.6	0.3	9	0.58	0.12

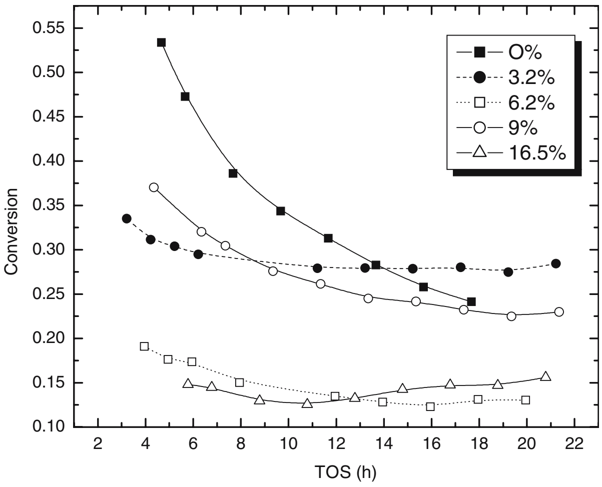

Figure 6. Variation of nickel load over catalysts HY-Zeolite, at WHSV= 0.09 l/h, T = 25 °C, P = 5 psig.

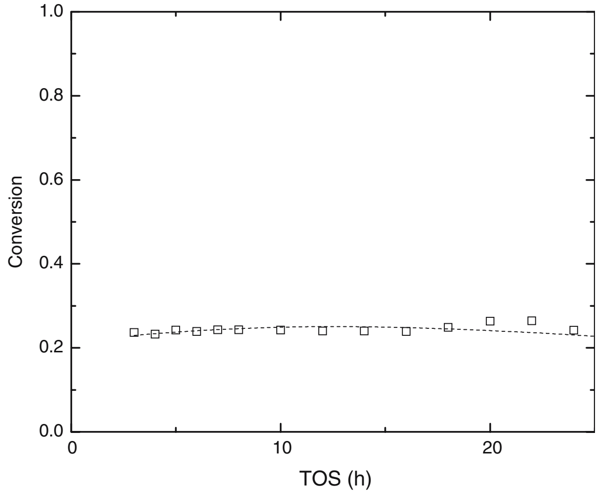

Figure 8. Stability test in a long duration run over HY-Zeolite with 9% load of nickel (catalyst B6). T = 25 °C, P = 4 psig, WHSV= 0.27 l/h.

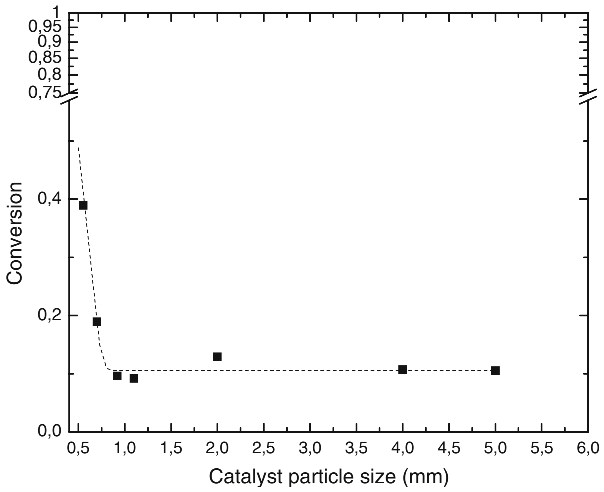

Figure 9. Conversion as function of particle size, catalyst HY-Zeolite with 9% of nickel load (catalyst 20), P = 4 psig, T = 25 °C, WHSV = 0.09 h^{-1}.

dimmers. We found a maximum in selectivity toward isooctene with B6, B7 catalysts, 3 and 6% of nickel load respectively (Figure 6). Though the conversion obtained over catalysts B6–B9 decreased slowly with time on stream, the selectivity toward isooctenes, the desired products, remained high, cracking products production was not observed (Figure 7).

Though the conversion obtained over catalyst B7 decreased slowly with time on stream (Figure 8), the selectivity toward isooctene, the desired product, remained high, conversion to cracking products was not observed.

Internal mass transfer resistances were minimized by using a particle size up to 0.7 mm as can be seen in Figure 9.

4. Conclusions

HY-Zeolite modified with nickel carbonate, designed as catalyst B2 showed high selectivity in oligomerization

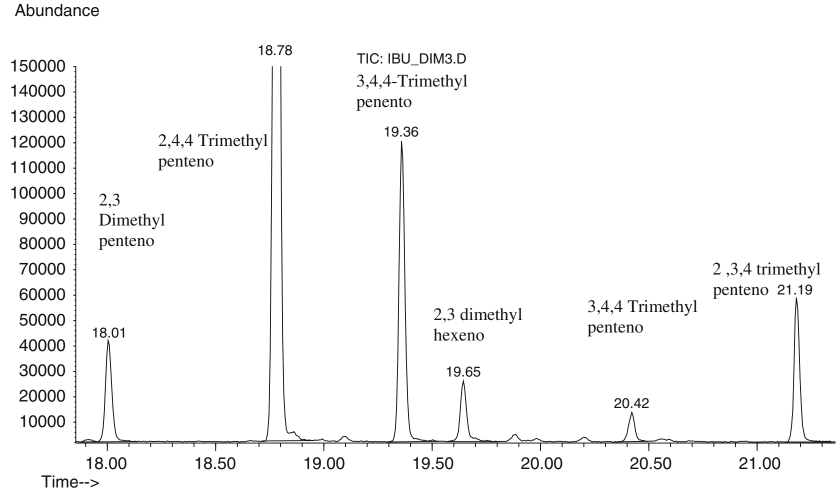

Figure 7. Typical chromatogram in isobutene dimerization reaction for B6 catalyst.

of isobutylene, addition of nickel resulted in an enhancement of acid sites total number. The activity of catalysts B2, B6 to B9, gave the best to perform gas phase reaction, so we proceeded to vary WHSV, i-C_4 flow, particle size, load of nickel, pressure and temperature to study the effect of these parameters over selectivity and activity. Nickel load between 3 and 6% showed the best selectivity to isooctene.

Dealumination of prepared catalysts as a result of nickel exchange was found the reason of acidity increment.

Progress in the development of adequate equipment for solid catalytic oligomerization is also needed, since a solid catalytic system often implies frequent catalyst deactivation.

References

[1] D. Kiessling, G. Wendt, K. Hagenau and R. Schoellner, Appl. Cat. 71 (1991) 69.

[2] R. Quann and F.J. Krambeck, Cat. Today 34(1997) 3.

[3] R. Alcántara, E. Alcántara, L. Canoira, M.J. Franco, M. Herrera and A. Navarro, 45 (2000) 19.

[4] M. Golombock and de Brujin, Ind. Eng. Chem. Res. 39 (2000) 267.

[5] S. Peratello, M. Molinari, G. Bellusi and C. Perego, Cat. Today 52 (1999) 271.

[6] Y. Medina (2003) Master's Thesis, Universidad Nacional Autónoma de México.

[7] R. Quann, L.A. Green, S.A. Tabak and F.J. Krambeck, Ind. Eng. Chem. Res. 27 (1988) 565.

[8] R.R. RamosPinto, P. Borges, M.A.N.D.A. Lemos, F. Lemos, J.C. Védrine, E.G. Derouane and F. Ramôa, Appl. Catal. A: General 284 (2005) 39.

[9] F.T.T. Ng and D.C. Creaser, Appl. Catal. A: General 119 (1994) 327.

[10] H. Hoang, Appl. Catal. A: General 114 (1994) 295.

[11] C. Flego, I. Kiricsi, W.O. Parker Jr. and M.G. Clerici, Appl. Catal. A 124 (1995) 107.

[12] H.B. Mostad, M. Stocker, A. Karlson and T. Rorvik, Appl. Catal. A 144 (1996) 305.