# Synthesis and Physicochemical Surface, and Catalytic Investigations of ZSM-11Treated with Small Amounts of Gold and Platinum

### Sahar. A. El-Molla<sup>a</sup>, Ibrahim. O. Ali<sup>b</sup> and Gamil, A. El-Shobaky<sup>c</sup>

<sup>a</sup> Chemistry Department, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt <sup>b</sup> Chemistry Department, Faculty of Science, Al-Azhar University, Nasser City, Cairo, Egypt <sup>c</sup> National Research Center, Dokki, Cairo, Egypt.

#### Abstract

ZSM-11 samples were synthesized and treated with small amounts of Pt and Au substrates (1 & 4wt% metal). The effects of this treatment on the structural, textural, and catalytic properties of the employed zeolite were studied. The acidity of Pt and Au-containing ZSM-11 solids was determined. The techniques employed were XRD, pyridine adsorption using FTIR-technique , N<sub>2</sub> adsorption at -196 °C, and catalytic conversion of isopropyl alcohol at 110-275 °C using a flow technique. The treatment of ZSM-11 with Au and Pt-species resulted in a structure collapse of 23, 19 %, respectively without much affecting its crystallite size. The specific surface areas of zeolites decrease slightly by treatment with Pt and Au species while their microporosity increased from 79 to 91%. All catalysts investigated behaved as selective dehydration solids having activities which increased by treating with Pt or Au species. The samples treated with 4 wt% Pt showed the biggest activity. The selectivity towards propene formation was also found to increase by treatment with Pt or Au species. **Keywords**: Zeolites, Pt , Au species, isopropyl alcohol conversion.

#### **1. Introduction**

Zeolites are effective adsorbents for hydrocarbons [1] acting as molecular sieve materials and considered as trapping materials for temporary storage of non-combusted hydrocarbons during the transient cold-start period in the catalytic treatment of automotive emissions [2,3]. Metal containing zeolites have been used as catalysts for a wide range of chemical reactions, such as dehydrogenation, oxidation, isomerization and cracking of various organic feed stocks [4]. Possible applications of these materials in various chemical industrial processes have attracted considerable interest to their investigations

Loading some metals on zeolites created bifunctional catalysts [5]. These catalysts were found to exhibit an improved selectivity for gasoline-range products [6]. It has been reported that metal loaded catalysts prepared by impregnation have lower selectivity to aromatics due to the decrease in the number of Brønsted acid sites on metal-containing zeolites. The dispersion of transition metals within the zeolite pore structures led to highly dispersed metal phase whose particle size will be limited to the pore dimension. As a result, the catalytic behavior of the supported catalyst is expected to be different from those with chunks of metals [4,7]. Metal loaded- zeolites have attracted much attention as they are interesting host-guest materials [8]. Gold ions are usually unstable and it is difficult to incorporate them by an ion-exchange method. Research on gold-loaded zeolites has been mainly focused on their applications as catalysts to remove harmful materials such as NO [9] CO [10]. ZSM-11 is currently of particular interest for aromatization of light alkanes. The treatment of ZSM-11 with Mo increases the concentration of acidic sites which catalyzing the oligomerization at high temperature. The presence of Lewis sites in Mo-ZSM-11 enhances dehydrogenation process of ethane into ethylene [11]. Fe-ZSM-11 catalysts have been reported to act as active and selective catalysts for the reduction of NOx [12].

Alcohol conversion is considered as a model test reaction of acidbase/redox properties of many catalysts. Meanwhile, such reactions produce a variety of products that having a vital industrial importance [13]. Among several groups of catalysts, noble metal-based materials [14,15], and zeolites [16] showed an interesting activity features. The conversion of alcohols is wellestablished reaction for the characterization of solid catalysts [17]. The dehydration of propan-2-ol was studied on HNaX, HNaY and dealuminated HYzeolites. The products of the reaction on acidic catalysts were confined to propene, diisopropyl ether, water and on basic catalysts is acetone. The Brønsted acidity of the zeolites is caused by acidic hydroxyl protons bonded at oxygen bridges( bridging OH groups) [18]. On acidic zeolites, propene has strong tendency to oligomerize [19]. The mechanism proposed was addition of propene on alkoxy species formed on Brønsted acid sites leads to the formation of alkanes with different chain lengths  $C_6H_{14}$ ,  $C_9H_{20}$ ,  $C_{12}H_{26}$  [20]

The present work aims at synthesis and characterization of ZSM-11 zeolite and studying the role of its impregnation with small amounts of Pt and Au species on the structure, textural, acidic and catalytic properties. The techniques employed were XRD, adsorption of pyridine using FTIR- technique, N<sub>2</sub>adsorption measurement at -196 °C and catalytic conversion of iso-propanol within 110-275 °C.

#### 2. Experimental

#### 2.1. Materials

The materials used were: silicic acid powder, sodium hydroxide pellets, aluminum sulfate  $Al_2(SO_4)_3.16H_2O$ , tetra butyl ammonium bromide (TBABr) and n-butyl amine, AuCl<sub>3</sub>, dichloro-tetraammine platinum ((NH<sub>3</sub>)<sub>4</sub>PtCl<sub>2</sub>) and commercial H<sub>2</sub>SO<sub>4</sub>. All the chemicals are of analytical grade and supplied by Merck company.

#### 2.1.1. Synthesis of NaZSM-11

Sodium form of ZSM-11 solid was synthesized hydrothermally. Silicic acid and aluminum sulfate were used as Si source and Al source, respectively. Concentrated sulfuric acid was used to adjust the gel pH. Tetra butyl ammonium bromide and n- butyl amine were used as template and a mobilizing agent for the synthesis of ZSM-11. The starting mixtures were formed using the following procedures [21]:

3.12 Na<sub>2</sub>O: 0.162 Al<sub>2</sub>O<sub>3</sub>: 6.185 SiO<sub>2</sub>: 0.185 TBABr: 100 H<sub>2</sub>O

Al<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O was first dissolved in a distilled water to get solution A, into which a 0.05 ml of concentrated H<sub>2</sub>SO<sub>4</sub> was added. TBABr Template, mobilizing agent, water and silicic acid form solution B. Pour solution A to B while stirring. After the addition was completed, the gel was stirred for at least 60 min to get a homogenous gel, and then the gel was transferred to a stainlesssteel autoclave and the sealed autoclave was placed in an air oven maintained at 150 °C for 4 days. The products obtained were washed with deionized water until the pH value of the washing water reached 8, and then dried overnight at 120 °C. The removal of organic template was carried out by heating at 550 °C for 6 h in air.

#### 2.1.2. Preparation of HZSM-11

The HZSM-11 was obtained by treating NaZSM-11 (synthesized in this work) three times with  $0.1M \text{ NH}_4\text{NO}_3$  solution (1 g zeolite in 100 ml) for 1h at room temperature. Between each step the sample was filtered and dried at 120°C for 4 h. The Sample was calcined by gradually increasing the temperature to 550 °C in air.

# 2.1.3. Preparation of Au/HZSM-11, Pt /HZSM-11 and Au-Pt/HZSM-11 by impregnation method

Au and/or Pt loaded zeolites were prepared by impregnation of HZSM-11 (synthesized in this work) with an aqueous solution of AuCl<sub>3</sub>, (NH<sub>3</sub>)<sub>4</sub>PtCl<sub>2</sub> or a

mixture of both to give 4 wt% Au, 4 wt% Pt or 1 wt% Au -4 wt% Pt, respectively. The volume of solution used was that necessary to ensure a complete wetness of the zeolite samples. The reaction temperature was 60°C for 4 h by using temperature controller type REX-P 90. After impregnation, the water was slowly allowed to evaporate at 110°C till dryness, and then the precursor sample was further dried at the same temperature for 6 h. The precursor sample was calcined at 300°C in air for 6 h. The obtained samples were referred as Au/HZ, Pt/HZ and Au-Pt/HZ, respectively. The colors of samples were black, white and dark brown, respectively.

#### 2.2. Characterization techniques

The X-ray diffractograms of various zeolitic samples were measured by using a diffractometer Bruker axs, D8 advance target. The patterns were run with Ni-filtered copper radiation ( $\lambda = 1.5404$  Å) with secondly momochromator at 40 kV and 40 m A with a scanning rate of 8° and 0.8 ° in 20 min<sup>-1</sup> for phase identification and line broading profile analysis, respectively purposes, automatic JCPDS library search, and match were used.

Nitrogen adsorption isotherms of various zeolitic adsorbents were measured at -196°C using conventional volumetric apparatus. Prior to the determination of the adsorption isotherm, the calcined sample (0.1g) was degassed for 3 h at 200°C under a reduced pressure of  $10^{-5}$  Torr in order to remove moisture and any possible adsorbent substrates. The specific surface area was obtained using the BET method while the micropore volume and the external surface area were obtained from the t-plot method. The "t-plot" method was applied in order to have another estimation of the microporous volume that can be determined by the method developed by de Boer *et al.*[22].

The acidity measurements of some selected solid samples were carried out using in situ FTIR spectra of the samples following the adsorption of pyridine was recorded with Bruker (Vector 22), single beam FT-IR 5300 spectrometer with 50 co-added scans at 2 cm<sup>-1</sup> resolution. The sample was pressed into a self-

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supporting wafer (ca. 30 mg/cm<sup>2</sup>) and mounted into a quartz infrared cell equipped with CaF<sub>2</sub> windows and an electric furnace. Prior to monitoring spectrum, the sample was heated at 200°C for 2h under a reduced pressure of  $10^{-5}$  Torr by linking the IR cell to a conventional closed vacuum Pyrex system with a dead volume of 300 cm<sup>3</sup>. A temperature controller connected to a thermocouple made of nickel chrome was used. Pyridine (5 Torr) was admitted into the cell and equilibrated with the sample for 30 min. Excess pyridine was then pumped off at 100 °C before recording the spectra at room temperature in the range of  $1700\sim1400$  cm<sup>-1</sup>. All the spectra were presented by subtraction of the corresponding background reference.

The catalytic activities of various catalysts were determined by using isopropyl alcohol conversion reaction in a flow reactor under atmospheric pressure at different temperatures varying between 100 and 275 °C. Thus, 100 mg for ZSM-11 catalyst sample was held between two glass wool plugs in a Pyrex glass reactor tube 20cm long and 1cm internal diameter packed with quartz fragments 2-3mm length. The temperature of the catalyst bed was regulated and controlled to within  $\pm 1$  °C. Nitrogen gas was used as the diluents and the isopropyl alcohol vapor was introduced into the reactor through an evaporator/saturator containing the liquid reactant at constant temperature of 35°C. The flow rate of the carrier gas (nitrogen) was maintained at 40 ml/min. Before carrying out such catalytic activity measurements each catalyst sample was activated by heating at 350°C in a current of, N<sub>2</sub> flowing at a rate of 40 ml/min. for 1 hour then cooled to the catalytic reaction temperature. The reaction products in the gaseous phase were analyzed chromatographically using Perkin-Elmer Auto System XL Gas Chromatograph fitted with a flame ionization detector. The column used was a fused silica glass capillary column type PE-CW length 15 m-1.0 UM Perkin-Elmer corp.

#### **3. Results and discussion**

#### 3.1. XRD investigation of different ZSM-11 zeolites

Figure 1 depicts diffractograms of untreated ZSM-11 sample and those treated with 4wt.% Pt and 4wt.% Au. It is clearly shown from Figure1 that the diffractograms given are characteristics of well-ordered ZSM-11 zeolite. XRD investigation showed that Au-or Pt-treatment of ZSM-11 did not much change the crystallite size of ZSM-11. The diffraction peaks of Pt and Au metals in the diffractograms having big relative intensities were detected showing well-ordered Pt and Au crystallites. The fact that the amounts of Pt or Au present in ZSM-11 samples were below the detection limit of x-ray diffractometer might suggest the enriched presence of these noble metals on top surface layers of the treated zeolites which should be much bigger than the nominal values (4 wt%). This finding is quite expected for solids prepared by impregnation method especially those prepared by using highly porous material such as zeolite and alumina [23].

The different structure characteristics of the investigated zeolites are cited in Table 1. Table 1 shows that the treatment of the investigated zeolite with 4 wt% Au led to a decrease of about 23% in its degree of crystallinity, as being evidenced from the decrease in peak area of the main diffraction line of zeolite. This decrease attained 19% in case of Pt-treatment. So, Pt or Au-treatment of ZSM-11 led to a measurable change in the structural characteristics of ZSM-11. This change might arise from the nature of both Pt and Au salts used in the impregnation process of zeolites. The computed values of Au and Pt-metal crystallite size in the investigated solids are 160 and 108 nm, respectively. This finding might suggest that Pt-metal is more dispersed than Au metal.

Incorporation of foreign cations in zeolite framework during its synthesis is known to cause some kind of structure collapse. The collapse is dependent on the nature and concentration of cation imbedded. It would be expected that incorporation of 4 wt% Pt or Au in zeolite framework during its synthesis might lead to a significant structure collapse of the treated zeolite. So, the method adopted (the impregnation method) in this work in treating ZSM-11 with Au or

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Pt species is recommended in order to have a limited structure collapse of zeolite that having excellent surface and catalytic properties.

#### **3.2. Surface characterization of various ZSM-11 zeolites**

The different surface characteristics of untreated ZSM-11 zeolite and those treated with Pt or Au were determined from a profound analysis of  $N_2$  adsorption data measured at -196°C over various adsorbents. Table 2 includes the different investigated surface characteristics. These characteristics include BET-surface areas  $S_{BET}$ ,  $S_t$  determined from the slope of what is called volume-thickness curve (V <sub>1-t</sub> plot) constructed using suitable standard t-curve depending on the constant in the BET equation.

Inspection of Table 2 shows the following: (i) The  $S_{BET}$  and  $S_t$  of various adsorbents are close to each other which justify the correct choice of t-curve used in pore analysis and also indicates the absence of ultra microspores. (ii) Both  $S_{BET}$  and  $V_p$  of the investigated zeolites were found to decrease slightly by impregnation with Pt or Au. (iii) The average pore diameter of ZSM-11 remains almost constant in all prepared solids. (iv)Pt or Au treatment of ZSM-11 decreased its external surface area and surface area of wide pores to about 32%. (v) The microporosity of the investigated ZSM-11 increased (15 %) upon treatment with Pt or Au. The observed decrease in its external surface area due to treatment with Pt or Au ran parallel to the observed increase in the crystallite size of ZSM-11 solids.

#### **3.3 Acidity measurements by Pyridine adsorption**

Figure 2 illustrates the in situ FTIR spectra of pyridine (Py) adsorption at 100°C followed by evacuation at the same temperature on the ZSM-11, Pt/ZSM-11, Au/ZSM-11 and Au+Pt/ZSM-11 samples. The spectrum of pyridine remained adsorbed on ZSM-11 after thermal evacuation at 100°C displayed bands at 1445 and 1598 cm<sup>-1</sup> characteristic of Lewis–coordinated pyridine [Lpy], whereas the bands at 1547 and 1635 cm<sup>-1</sup> are due to Brønsted–coordinated pyridine (Bpy). The assignment of these bands was in agreement

with those given by Parry [24]. The band at 1490  $\text{cm}^{-1}$  is due to Lewis and Brønsted-coordinated pyridine (Lpy + Bpy).

The in situ FTIR spectra of pyridine chemisorbed on Pt/ZSM-11 or Au/ZSM-11 or both of them after being evacuated at 100°C were characterized by Lpy at 1445 and 1598 cm<sup>-1</sup>, and by Bpy at 1547, 1635 cm<sup>-1</sup>. It is clearly shown that the area of the band at 1547 cm<sup>-1</sup> relative to Brønsted acid sites increased after treatment with Au or Pt or both. On the other hand, the amount of Lewis acid sites at 1445 cm<sup>-1</sup> decreased in the same sequence. Such decrease is presumably caused by the coordination to aluminum [25].

The concentration of the Brønsted acid sites (BAS) and Lewis acid sites (LAS) were estimated based on intensities of the bands found at 1547 and 1445 cm<sup>-1</sup>, taking the corresponding molar extinction coefficients ( $\epsilon$ ), i.e., 0.059  $\pm$ 0.004 and 0.084  $\pm$ 0.003 cm<sup>2</sup>/mol, respectively [26,27]. Quantitative data were calculated using the Lambert-Beer equation [28,29] listed in Table (3). It is clearly shown from Table (4) that Au and Pt-treatment much increased Brønsted acid sites concentration and decreases effectively the Lewis acid sites concentration. The coexistence of both Pt and Au affected a measurable decrease of 35 % in the total acid sites concentration, which decreased slightly in the presence of Au or Pt metals.

## 3.4 Catalytic conversion of isopropyl alcohol carried out over different ZSM-11 treated with Pt and Au species

The catalytic conversion of isopropanol was carried out over ZSM-11 and samples treated with Pt and / or Au species. The reaction was carried out using a constant flow rate at temperature varied between 110 and 275 °C. Figure 3 shows the catalytic activity expressed as, total conversion of isopropanol as a function of the reaction temperature.

Figure 3 shows that: (i) The catalytic activity increases with increasing the reaction temperature. (ii) The catalyst treated with 4 wt% Pt measured the biggest catalytic activity and the coexistence of (4 wt% Pt, 4 wt% Au) did not

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exert any measurable effect on the catalytic activity. The increase was, however, more pronounced in case of treatment with 4 wt% Pt-1 wt% Au. The observed measurable increase in the catalytic activity of ZSM-11 due to treatment with Pt and Au could be attributed mainly to the recorded outstanding increase of the Brønsted acid sites concentration involved in the catalytic conversion of alcohol investigated.

The fact that the induced increase in the Brønsted acid sites concentration is slightly smaller in case of Pt than that of Au might suggest that other parameter together with acidity might be responsible for the observed results. In fact, it has been reported in XRD section in this work that the structure collapse of ZSM-11 due to Au-treatment is bigger than the collapse observed in case of Pt-treatment.

The selectivity of the investigated solids towards propene(Sp), acetone(Sa) and Oligomerization products(So) at various reaction temperatures (110 - 275 °C) were calculated and given in Figure 4 and Table 4. Inspection of Table 4 shows the following: (i) All the investigated solids behaved as dehydration catalysts producing propene. The selectivity increases with increasing the reaction temperature till a maximum limit above which the selectivity, towards propene tends to decrease. (ii) The selectivity for propene formation increases in case of Pt or Au treatment. The measurable significant drop in the dehydration selectivity of various investigated solids at high reaction temperatures might be attributed to a possible formation of other products.

The formation of propene depends on the acid centers (by  $E_2$  – mechanism) in which there are synchronous elimination of  $\beta$ -hydrogen in iso-propanol and hydroxyl groups to the catalyst surface [30]. Several authors claimed that, acetone production depends on the presence of basic centers [31]. Many studies showed that, alcohol interacts with solid catalyst via adsorption with subsequent formation of alkoxide [32] through adsorption on  $M^{+n}$  —  $O^{II}$  sites or by

interaction of alcohol with residual surface OH - groups [33]. Formation of propene took place according to [32]



Scheme 1. Acid-base dehydration model of 2-propanol (propene formation).

The acetone formation proceeds also via the following mechanism [32]





In fact, it has been reported that at high temperature above 200°C propene underwent an oligomerization process [20, 34-36]. Many studies showed that propene has a tendency to oligomerize on acidic zeolites to give alkanes with different chain length [20,34]. Other study showed oligomerization of olefins can accelerate undesirable side reactions (cracking, coke formation....etc). It was found that cis and trans 3- hexene is produced in oligomerization of propene in presence of acid catalyst [35]. It has been also reported that H- Mordenite catalyst has a tendency to readsorb olefins in the pores to form oligomerization products as evidenced from formation of cyclopentadienyl cation during TP process of 2-propanol showing occurrence of coking *i.e.* formation of high molecular weight species and formation of saturated alkyl chains [36].

The oligomerization may took place via the following scheme [20]



**Scheme 3.** Conversion of 2-propanol and oligomerization of produced propene.

Determination of the apparent activation energy  $\Delta E$  of the catalytic conversion of isopropyl alcohol yielding propene in presence of pure and treated ZSM-11 with Pt and or Au species system has shed some light on the possible changes in the mechanism of the catalyzed reaction. The values of reaction rate constant (k) measured at different reaction temperatures ranged from 100 to

140°C over the variously treated solids have allowed  $\Delta E$  to be obtained via direct application of the *Arrhenius* equation. The values of  $\Delta E$  thus obtained are listed in Table 5. Also included in Table 5 are the values of *ln* A (frequency factor in the *Arrhenius* equation) calculated for investigated catalysts.

Inspection of the data listed in Table 5 reveals the following: (i) Treatment of ZSM-11 catalyst with Au and /or Pt species brought about a decrease in the value of  $\Delta E$ . This finding ran parallel to the observed progressive increase in the catalytic activities of the investigated solids due to treatment of ZSM-11 catalyst with Au and /or Pt species. (ii) It can also be seen from Table 5 that ln A showed some fluctuations indicating a compensation effect and surface heterogeneity of these solids.

This finding justifies the recalculation of the values of  $\Delta E$  for the reaction conducted over different investigated solids adopting the values of ln A of the pure specimens to the other noble metals-treated samples calcined at the same temperatures.  $\Delta E^*$  values were obtained, the computed  $\Delta E^*$  values are given in the last column of Table 5. The comparison of  $\Delta E^*$  values for pure and various treated solids calcined at the same temperatures showed that treatment of ZSM-11 catalyst with Au and/or Pt did not modify the values of activation energy of the catalyzed reaction. In other words, treatment of ZSM-11 catalyst with Au and /or Pt species did not modify the mechanism of catalytic conversion of isopropanol but alters the concentration of catalytically active constituents.

#### 4. Conclusions

The main conclusions that may be drawn from the results obtained are as follows:

 ZSM-11 sample was successfully synthesized and treated Pt, Au species. Pt- and Au- treatments of the prepared ZSM-11 samples have been followed up by impregnating a known amount of zeolite sample with solutions containing calculated amounts of AuCl<sub>3</sub> or (NH<sub>3</sub>)<sub>4</sub>PtCl<sub>2</sub> followed by drying and calcination in air at 300 °C.

- Pt and Au-treatment of ZSM-11 resulted in a limited structure collapse of 19 and 23 %, respectively without much affecting its crystallite size.
- 3. The BET- surface area of ZSM-11 decreased slightly by treatment with Pt or Au with subsequent increase in its microporosity.
- The Brønsted acidity of ZSM-11 was much increased by treatment with Pt or Au.
- 5. All catalysts investigated behaved as selective dehydration solids having activities which increased by treatment with noble metals.

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	Peaks are	as(a.u.) o	f main diff	erent pea	iks at	Collapse 4 Å %	Average	Crystallinity	
Samples	11.13 Å	9.99 Å	<b>3.84</b> Å	3.72 Å	<b>3.34</b> Å		(nm)	Intensity Count	Intensity %
HZSM-11	639	366	628	351	163		56	429	100
Au/ZSM-11	552	298	455	231	124	23	50	332	77
Pt/ZSM-11	587	314	471	250	119	19	50	348	81
Au+Pt/ZSM-11	447	251	428	214	103	33	49	287	67

**Table1:** Peak areas of the main diffraction lines of various zeolites, average crystallite size and crystallinity of the investigated solids calcined at 550 °C

Sample	S <sub>BET</sub> (m²/g)	$S_t$ (m <sup>2</sup> /g)	Vp <sup>total</sup> (cm <sup>3</sup> /g)	r <sup>—</sup> (Å)	S <sup>μ</sup> (m²/g)	S <sup>ext</sup> (m <sup>2</sup> /g)	S <sup>wid</sup> (m²/g)	V <sub>p</sub> <sup>μ</sup> (cm <sup>3</sup> /g)	V <sub>p</sub> <sup>wid</sup> (cm <sup>3</sup> /g)	Microp. %	C.const
HZSM-11	567	542	0.527	23.26	495	52	72	0.461	0.067	79	49
Au/ZSM-11	528	526	0.467	22.11	481	62	47	0.425	0.042	91	105
Pt/ZSM-11	534	516	0.486	22.74	481	35	53	0.438	0.048	90	50
Au+Pt/ZSM-11	509	472	0.487	23.92	453	38	56	0.433	0.054	89	52

 Table 2: Some Surface characteristics of ZSM-11 adsorbents treated with 4wt% Pt or Au and samples treated with 4wt% Pt+1wt % Au.

## **Table 3:** Quantitative results of total amount of acid sites accessible to pyridine

Sample	Temperature	Number o (μm	f Active sites 10le/g)	[ <b>B</b> ]/[] ]	Total of acid sites		
	°C –	$[L]^a$	$[B]^b$	נשוינען	(µmor/mg)		
ZSM-11	100	55	2.5	0.046	57.52		
Pt/ZSM-11	100	40.1	11.2	0.28	51.30		
Au/ZSM-11	100	39.2	13.2	0.34	52.40		
Pt+Au/ZSM-11	100	25.4	12.2	0.48	37.60		

and relative B/L in the different samples

a = Lewis acid sites

b = Brönsted acid sites.

Temperature (°C)	Solid Catalyst											
	ZSM-11		2	4 % Pt		4 % Au			1%Au-4 % Pt			
	Sp	Sa	So	Sp	Sa	So	Sp	Sa	So	Sp	Sa	So
100	55	45.8	0.2	55	44.8	0.2	68.4	31.4	0.2	80.0	19.8	0.2
110	58	42.8	0.2	65	34.5	0.5	82.0	17.6	0.4	90.0	9.7	0.3
120	66	33.7	0.3	83	16.3	0.7	88.5	10.9	0.6	91.0	8.5	0.5
130	73	26.7	0.3	89	10.0	1.0	92.0	7.2	0.8	93.5	6.0	0.5
140	75	24.4	0.6	94	4.8	1.2	94.0	5.1	0.9	95.0	4.3	0.7
175	89	10	1.0	98	0.9	1.5	98.3	0.4	1.3	98.4	0.3	1.3
200	98	0.5	1.5	96.5	0.1	3.4	97.6	0.4	2.0	97.7	0.3	2.0
225	96	0.5	3.5	87.1	0.1	12.8	93.4	0.4	6.2	91.8	0.3	7.9
275	70	0.5	29.5	68.0	0.1	31.9	65.2	0.4	34.4	72.4	0.3	27.3

**Table 4:** Effect of treatment ZSM-11 with Au and/or Pt species on the products selectivities.

#### Note:

Sp: selectivity towards propene formation (dehydration),

Sa: selectivity towards acetone formation (dehydrogenation) and So: selectivity towards oligomerization

solid	∆ E kJ/mol	ln A	$\Delta \mathbf{E}^{\star}$ kJ/mol
ZSM-11	140.12	35.82	140.12
4%Au	137.45	36.24	139.0
4%Pt	120.7	30.87	136.0
1%Au-4%Pt	109.0	27.29	135.0

**Table 5:** Activation energy  $\Delta E$ ,  $\Delta E^*$  frequency factor for propene formation forZSM-11 and thattreated with Au and/or Pt species in catalytic conversion of isopropanol.





2θ degree



Wavenumber/cm<sup>-1</sup>



