Determination of Lewis and Brönsted acid sites by gas flow-injection technique

Malik Musthofa[1], Ainul Hakimah Karim[1], Nurrulhidayah Ahmad Fadzlillaah[1], Nur Hazirah Rozali Annuar[1], Aishah Abdul Jalil[2], Sugeng Triwahyono[1]*

[1]Ibnu Sina Institute for Fundamental Science Studies, [2]Department. of Chemical Engineering, Faculty of Chemical Engineering Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

ABSTRACT

Gas flow-injection technique pyridine-FTIR was studied for determination of Lewis and Brönsted acid sites on the solid super acid catalysts. The system consists of stainless steel gas cell which can be heated up to 623 K, CaF2 windows, pyridine injection port and double liquid nitrogen trap for removal of moisture. Pure nitrogen gas and pyridine were used as a carrier and probe molecule. Pyridine was injected to the sysem at 423 K followed by flushing of N_2 gas through double liquid nitrogen trap at 423 for 1 h and at 573 K for 30 min. All spectra were recorded at room temperature. This technique gave similar results to those of taken by vacuum system for HZSM-5, Pt/SO_4^{2-}-ZrO_2, Al_2O_3 catalysts.

/ Gas flow technique | Pyridine | Lewis acid sites | Brönsted acid sites | HZSM-5 | Pt/SO_4^{2-}-ZrO_2 | Al_2O_3 |

1. INTRODUCTION

Solid acid catalysts have found significant role on the development of more efficient and environmentally friendly chemical technologies [1]. Measurement of their surface acidity therefore is of great interest. Several techniques have been proposed to provide information on the type and acidity of solid catalysts for more understanding in the properties of solid catalyst. Among these techniques, conventional pyridine infrared spectroscopy is the easiest and most direct method to identify the Lewis and Bronsted acid of solid catalysts [2-6].

Since the large application and the experimental reasons, in situ apparatus of IR spectroscopy of pyridine adsorption was successfully extensively developed. However, this technique apparatus is commonly designed for vacuum system which needs critical skills and equipments as well the long time analysis [7]. Consequently, flow technique of IR spectroscopy of pyridine adsorption was suggested as more simple technique apparatus which allow the work was performed more efficiently. Although this technique was applied by some researchers [8-9], the detail investigation of this technique compared to vacuum one is still lack. In the present paper, we report the results of flow system IR of pyridine adsorption to determine the Bronsted and Lewis acid sites on solid acid catalysts.

Corresponding author at: Ibnu Sina Institute for Fundamental Science Studies Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia E-mail address: sugeng@ibnusina.utm.my (Sugeng Triwahyono)

2. EXPERIMENTAL

2.1 Preparation of catalyst

A commercial HZSM-5 (Zeolyst) with Si/Al atomic ratio of 80 was used as a zeolitic sample. The HZSM-5 contains only protonic acid sites after treatment at 773 K. The sulfate ion-treated $Zr(OH)_4$ sample was prepared by impregnation of $Zr(OH)_4$ (Aldrich) with 1N H_2SO_4 (Merck) aqueous solution, followed by filtration and drying at 383 K overnight. The sulfated zirconia, SO_4^{2-}-ZrO_2 was obtained by calcinations of SO_4^{2-}-$Zr(OH)_4$ at 873 K for 3 h in air. The Pt/SO_4^{2-}-ZrO_2 was prepared by impregnation of the SO_4^{2-}-ZrO_2 with an aqueous solution of H_2PtCl_6, (Merck) followed by calcinations at 873 K for 3 h in air. The content of Pt was 0.5 wt %.

2.2 Characterization of catalyst

The crystalline structure of samples were determined with a Bruker AXS D8 Automatic Powder Diffractometer using Cu Kα radiation with λ= 1.5418 Å at 40 kV and 40 mA, over the range of 2θ = 0 - 40°. Fourier transform infrared (FTIR) analysis of the samples was performed with a Perkin-Elmer Spectrum GX FT-IR Spectrometer using KBr discs, in the range 4000-400 cm^{-1}. The surface area of the sample was determined by Quantachrome Autosorb-1 at 77 K. Prior to the measurement, the sample was outgassed at 573 K for 3 h.

2.3.   Pyridine adsorption procedure

Figure 1 illustrates the schematic diagram of gas flow-injection technique for adsorption of pyridine on solid material.   The adsorption procedures are as follows. A self-supported wafer placed in an in-situ stainless steel cell IR cell with CaF_2 windows was heated in a nitrogen gas flow at 623 K for 3 h. Then, the sample was exposed to the pyridine at 423 K for 1 h followed by flushing of nitrogen gas at 573 K for 30 min.   Nitrogen gas was dried by molecular sieve and double liquid-nitrogen traps. All spectra were recorded at room temperature.
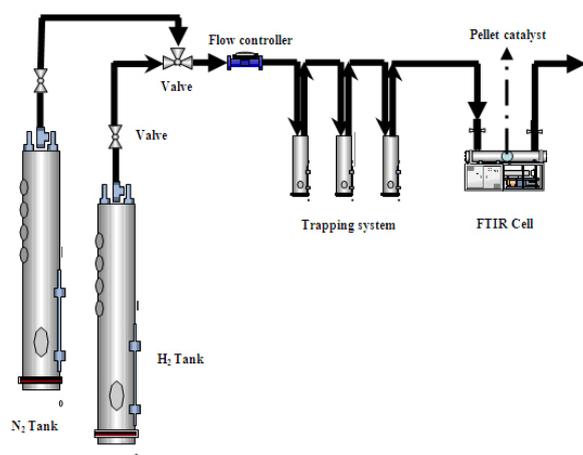

Fig. 1 : Schematic diagram of gas flow-injection technique.

3.   RESULTS & DISCUSSION

3.1.   Characterization of the catalyst

The specific surface area of HZSM-5, Pt/SO_4^{2-}-ZrO_2, Al_2O_3 catalysts were 345, 110 and 190 m^2/g, respectively. The diffractogram of HZSM-5 is shown in Figure 2. The XRD result indicated the high crystallinity of the sample. Significant peaks which corresponding to the specific peaks of ZSM-5 was observed in the range of 2θ = 7-10° and 22-25° [10]. Figure 3 shows the XRD pattern of Pt/SO_4^{2-}-ZrO_2 (PSZ). The PSZ sample displayed two well-established polymorphs of monoclinic and tetragonal phases. The peak at about 2θ = 30° is assigned to tetragonal phase of zirconia, and the peaks at about 2θ = 28°, 32°, and 35° are assigned to monoclinic phase of zirconia. The peaks at about 2θ = 40° and 2θ = 45° corresponding to Pt (111) and Pt (200) are not observed which indicated that the amount of Pt is too small for mass analysis [11]. Although it is not shown here, the amorphous structure was observed for Al_2O_3 sample.

Figure 4 presents the FTIR spectrum of HZSM-5. Significant absorption bands are observed at 1225, 1100, 795, 545 and 450 cm^{-1}. Absorption bands at 1225 and 1100 cm^{-1} are corresponding to the external and internal asymmetric stretching vibration of TO_4 tetrahedral respectively. The absorption band at 795 cm^{-1} is assigned to the external symmetric stretching vibration while the band

observed at 545 cm^{-1} indicated the vibration of double five member-rings by tetrahedral SiO_4 and AlO_4 units. The 450 cm^{-1} absorption band is attributed to internal vibration of Si and AlO_4 tetrahedral. The existence of bands at 450, 545, 795, 1100 and 1225 cm^{-1} are indicating the complete crystalline structure of ZSM-5 which is parallel to the XRD results [10].
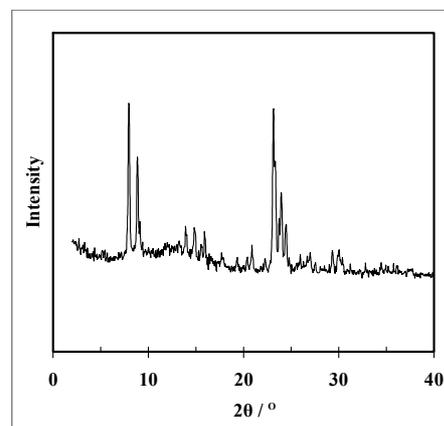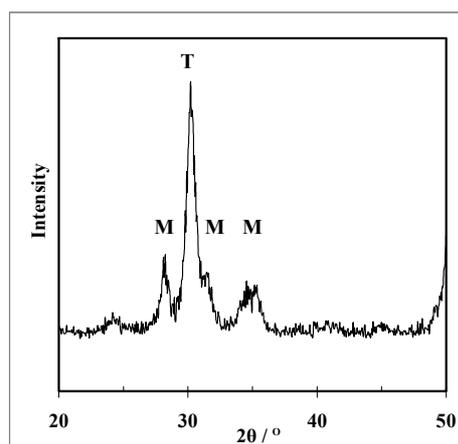

Fig. 2 : XRD pattern of HZSM-5.

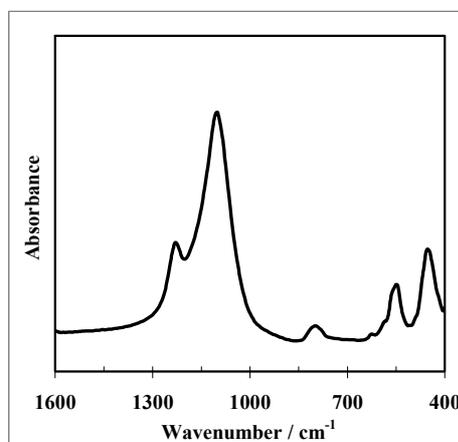**Fig. 3 :** XRD pattern of Pt/SO_4^{2-}-ZrO_2.

Fig. 4 :   FTIR spectrum of HZSM-5 .

FTIR spectrum of PSZ is displayed in Figure 5. The sample showed a strong peak at 1395 cm^{-1} which is assigned to the asymmetric S=O stretching mode of sulfated groups bound by bridging oxygen atoms to the surface. Two other bands at 1025 and 1040 cm^{-1} are assigned to the asymmetric stretching frequencies of the S-O bonds [12].

3.2. The acidity of sample

Figure 6 shows the spectra of adsorbed pyridine on HZSM-5 measured by vacuum and flow techniques. The absorption bands at 1455, 1545 and 1490 cm^{-1} are due to pyridine adsorbed on Lewis acid site (L:Py), Brönsted acid site (B:Py), and on both acid sites ((B+L):Py) [13]. The result clearly revealed the similarity of the results measured by vacuum and flow techniques.
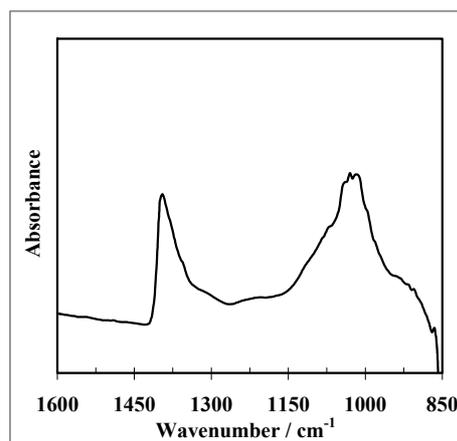
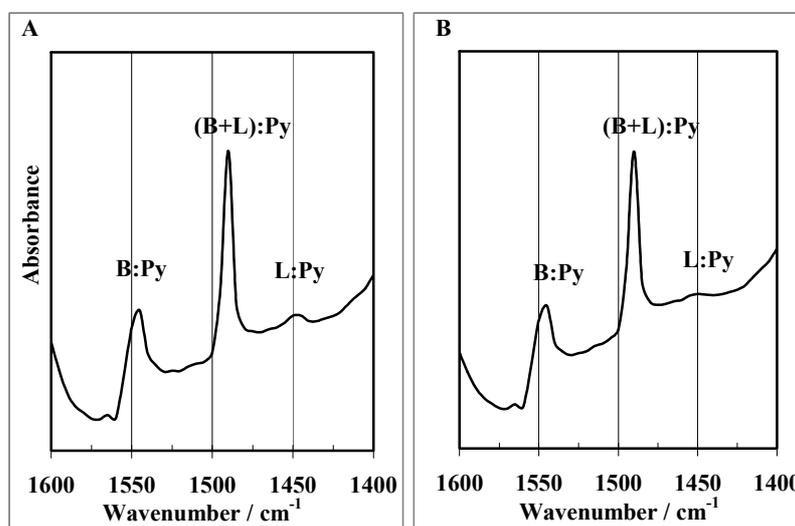**Fig. 5 :** FTIR spectrum of $Pt/SO_4^{2-}-ZrO_2$.

Fig. 6 : IR spectra of pyridine adsorbed on Zn/HZSM-5 for (A) vacuum system and (B) flow system.

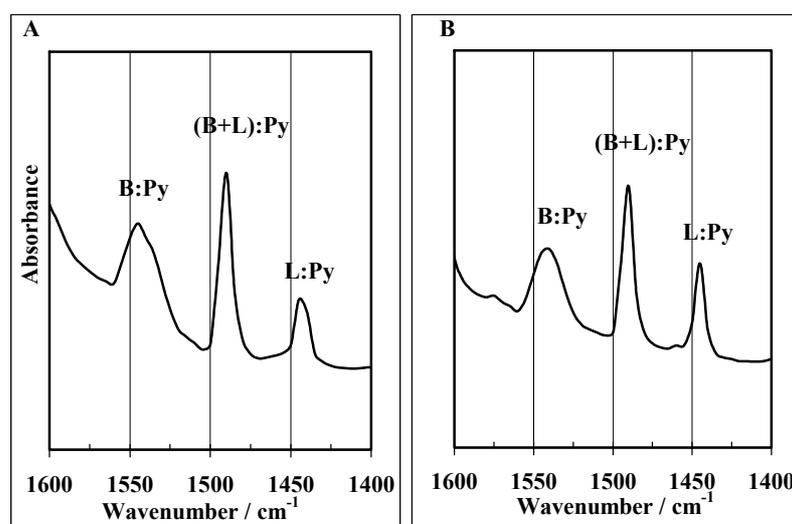**Fig. 7 :** IR spectra of pyridine adsorbed on $Pt/SO_4^{2-}-ZrO_2$ for (A) vacuum system and (B) flow system

**Table 1 :** Acid sites fraction of HZSM-5.

Catalysts	Vacuum system		Flow system	
	Fraction of acid sites			
	Brönsted	Lewis	Brönsted	Lewis
HZSM-5 (Si/Al=80)	0.89	0.11	0.92	0.08
HZSM-5 (Si/Al=90) [14]	0.9	0.1	-	-
HZSM-5 (Si/Al=49) [15]	0.72	0.28	-	-
HZSM-5 (Si/Al=37) [16]	0.69	0.31	-	-

More obvious observation would be found by calculating the fraction of acid sites on solid acid catalyst. The fraction of acid sites on solid catalysts can be estimated by method described in the literature [14]. The fraction of Brönsted and Lewis acid sites of the sample measured by vacuum technique are 0.89 and 0.11, while those measured by flow technique are 0.92 and 0.08 respectively. The results gave a good agreement with previous report by Takahara *et al.* [14]. They estimated the fraction of Brönsted and Lewis acid sites of HZSM-5 were 0.9 and 0.1. However, several papers pointed out the different value of fraction of acid sites on HZSM-5 as described in Table 1 [15-17]. The differences may be caused by the difference of silica alumina ratio of HZSM-5. On the rising of silica alumina ratio, the fraction of Brönsted acid sites rose while the fraction of Lewis acid sites decreased. It can be due to a

higher stability of HZSM-5 as the silica alumina ratio increases, which hinders the dehydroxylation of Brönsted acid sites [14].

The spectra of adsorbed pyridine on PSZ measured by vacuum and flow techniques are showed in Figure 7. The results showed that there are no significant differences on the Lewis and Brönsted acid site peaks for both techniques. The fraction of Brönsted and Lewis acid sites of PSZ measured by vacuum technique are 0.55 and 0.45, while those measured by flow technique are 0.44 and 0.56. The values are close to those reported by Stevens *et al.* [8] which the fraction of Brönsted and Lewis acid sites of PSZ are 0.46 and 0.54, respectively. However, other researchers [18-19] reported the different values for fraction of acid sites of PSZ as described in Table 2. The differences may be influenced by the differences in the evacuation temperature and/or time. By increasing the evacuation temperature and/or time, pyridine molecules adsorbed on weak acid sites should be desorbed while those adsorbed on strong acid sites could be retained. The PSZ results in this experiment indicated that Lewis acid sites are strong enough to retain pyridine against evacuation at high temperature, while there is a considerable number of weak Brönsted acid sites from which adsorbed pyridine is desorbed by evacuation at high temperature. Therefore the fraction Brönsted acid sites drastically decreased as the evacuation temperature was raised [5].
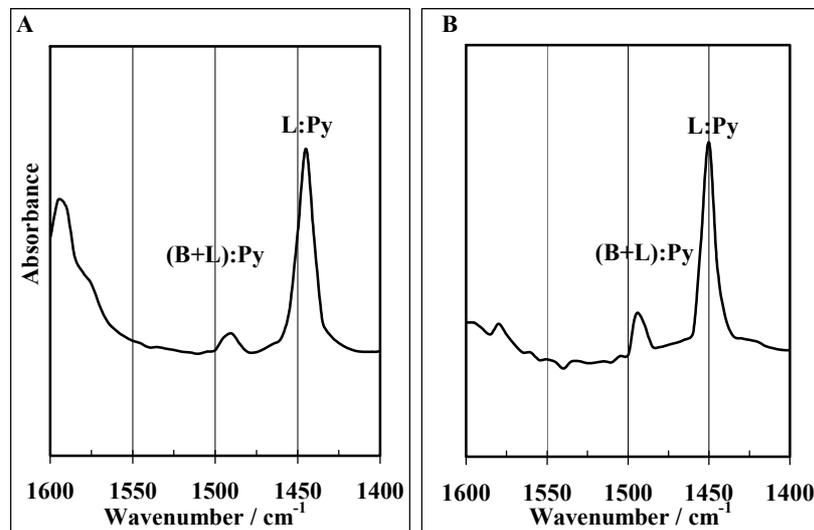
Fig. 8 : IR spectra of pyridine adsorbed on Al_2O_3 for (A) vacuum system and (B) flow system.

The extinction coefficient ratio of Brönsted to Lewis acid sites for HZSM-5 and PSZ were 1.49 and 1.69 respectively. The ratio of extinction coefficient at bands 1454 and 1545 cm^{-1} was determined by converting the bands at 1454 cm^{-1} to the band at 1545 cm^{-1} by addition of a small quantity of water. The obtained value is different with our previous report for HZSM-5 and Pt/WO$_3$-ZrO$_2$

which the extinction coefficient of ratio were 1.1 and 1.82 respectively [5,15]. This difference may be resulted by the differences between the integrated absorbance and the absorbance at the peak position.

We have also applied gas flow-injection technique for pyridine adsorption FTIR to measure the acidity of Al_2O_3 (AKP50 Sumitomo Chemical Co., Japan). Figure 8

reveals the spectra of adsorbed pyridine on Al_2O_3 measured by vacuum and flow techniques. As can be seen, both techniques provide alike results which have a great intensity of Lewis acid site with the absence of Brönsted acid site. The intensity ratio of absorption bands at 1455 and 1490 cm^{-1} are 5.38 and 4.71 for vacuum and flow techniques, respectively. The similar values were also reported in several literatures [19-20].

Table 2 : Acid sites fraction of Pt/SO_4^{2-}-ZrO_2.

Catalysts	Temperature of Evacuation / K	Vacuum system		Flow system	
		Fraction of acid sites			
		Brönsted	Lewis	Brönsted	Lewis
PSZ	523	0.55	0.45	0.44	0.56
PSZ [8]	423	-	-	0.46	0.54
PSZ [18-19]	673	0.28	0.74	-	-

Based on the results of HZSM-5, PSZ and Al_2O_3, the gas flow-injection technique was acceptable technique for determination of acidic sites of solid materials.

Furthermore, this technique gives important advantages as compared to vacuum system, such as simple apparatus, easy in handling, and short time analysis.

4. CONCLUSION

Gas flow-injection technique pyridine FTIR was developed to determine Lewis and Brönsted Acid sites of solid catalysts. This technique gave a similar results with the results measured by conventional vacuum technique. This technique gives several advantages such as simple apparatus, short time analysis and easy in handling and experiment.

ACKNOWLEDGEMENT

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