Analysis Si/Al ratio in zeolites type FAU by laser induced breakdown spectroscopy (LIBS)

W A Contreras, R Cabanzo and E Mejia-Ospino

Laboratorio de Espectroscopia Atómica y Molecular (LEAM) Universidad Industrial de Santander, Escuela de Física, Facultad de Ciencias. Universidad Industrial de Santander (UIS). AA. 678 Bucaramanga-Colombia

E-mail: emejia@uis.edu.co

Abstract. In this work, Laser Induced Breakdown Spectroscopy (LIBS) is used to determine the Si/Al ratio of Zeolite type Y. The catalytic activity of zeolite is strongly dependent of the Si/Al ratio. We have used Si lines in the spectral region between 245-265 nm to determine temperature of the plasma generated on pelletized sample of zeolite, and stoichiometry relation between Si and Al.

1. Introduction

Laser Induced Plasma Spectroscopy (LIPS or LIBS) is an alternative elemental analysis technique based on the study of emission spectra of plasmas produced by the interaction of high-power laser beam with gas, solid and liquid samples. The increasing popularity of this technique is due to the ease of the experimental set-up and to the wide flexibility in the investigated material that does not need any pre-treatment of the sample before the analysis [1].

In the catalysts family, environmentally friendly and noncorrosive, solid acid catalysts (zeolites and zeolite-based catalysts) for the number of petrochemical processes have been under interest over the past decade. The mechanism of hydrocarbon conversion inside zeolites is quite complex, as a significant number of different types of competing chemical reactions occur. However is known that the catalytic activity of zeolite is strongly dependent of the Si/Al ratio. Techniques as X-ray diffraction (XRD) and, $^{29}$Si and $^{27}$Al magic angle spinning nuclear magnetic resonance are generally used to characterize the Si/Al ratio [2-5].

In this work, Laser Induced Breakdown Spectroscopy (LIBS) is used to determine the Si/Al ratio of zeolite type Y. In order to measure Si/Al ratio by LIBS is necessary to know the temperature of laser-induced plasma, for this we have used lines of Si(I) in the spectral region between 245-265 nm. In addition, we have used the lines 298.76 and 308.22 nm of Si and Al, respectively, to determine the Si/Al ratio in the zeolite sample studied here.

To whom any correspondence should be addressed.
2. Experimental

The second harmonic from a Q-switched Nd:YAG laser (532 nm, 10 ns) is focused through a quartz lens (f ~ 100 mm) on the pelletized sample of zeolite surface within the discharge chamber, inducing the formation of a transient plasma plume in argon atmosphere. The plasma emission is focused through a quartz lens (f ~ 50 mm) and collected with a quartz optical fiber, and introduced into a 0.5 m Czerny-Turner spectrograph (Shamrock 500 Imaging, Andor Technology). A 1800 grooves/mm diffraction grating (spectral resolution 0.075 nm, dispersion 0.83 nm/mm) is used to disperse the emission spectrum, which is projected on the image plane of the spectrograph and recorded on an Intensified Charge Couple Device (ICCD) detector with an array of 1024×256 pixels (ICCD) detector (iStar DH720, Andor Technology). The laser energy, delay time and integration time gate were 70 mJ/pulse, 2 μs and 10 μs, respectively. The schematic diagram of our LIBS experimental setup is depicted in Fig. 1. The zeolite Y was obtained from Zeolyst International, with commercial name of Zeolite Y CBV-720, and SiO$_2$/Al$_2$O$_3$ mole ratio of 30.

![Experimental setup by laser plasma.](image)

3. Results and discussion

Figure 2 shows spectral region between 245 and 265 nm, used to determine plasma temperature with several Si(I) lines 250.69, 253.24 and 263.13 nm. For the compositional analysis of Si/Al ratio of zeolite, we looked for a spectral region containing emission lines of both Si and Al (Fig. 3). The spectra obtained were measured by accumulating (10 μs) the plasma emission corresponding to a single shot laser. Assuming local thermodynamic equilibrium (LTE) and optically thin conditions, the measurements of intensity of emission lines coming from the laser-induced plasma can be used to check the composition (Eq. 1) and the ratios of atomic concentrations among the plasma species (Eq. 2). The plasma elemental composition reflects the target composition [6-8].

$$k_i = \frac{e^2 \lambda_0^2}{4e_0 mc^2} \int f_k g_i e^{\frac{E_i}{kT}} Z(T) \left(1 - e^{-(E_i - E)} / kT \right)$$

$$\frac{I_{Si}}{I_{Al}} = \frac{k_{i, Si} N_{Si}}{k_{i, Al} N_{Al}}$$

![Figure 1.](image)
Where $\lambda_0$ is the central wavelength (m) of the emission line, $f_{ik}$ the transition oscillator strength (dimensionless), $g_i$ the degeneracy (dimensionless) of the lower energy level, $E_i$ and $E_k$ the energies (J) of the lower and upper energies levels, respectively, $k$ the Boltzmann’s constant (JK$^{-1}$), $T$ the absolute temperature (K), $Z(T)$ de partition function (dimensionless), $e$ the elementary charge (C), $\varepsilon_0$ the permittivity of free space (Fm$^{-1}$), $m$ the electron mass (kg) and $c$ is the speed of light in vacuum (ms$^{-1}$). $I_{Si}$ and $I_{Al}$ are the integrated intensity of the spectral line emitted by Si and Al species, respectively, in optically thin conditions; $N_{Si}$ and $N_{Al}$ are the number density of the emitting species.

In order to calculate $k_{t, Si}$ and $k_{t, Al}$ coefficients is necessary to know the plasma temperature. In order to measure the laser-induced plasma temperature at the energy per pulse laser used here, we have assumed local thermodynamic equilibrium (LTE) condition [6-8]. In this condition the electrons dominate the reaction rate, so the measured intensity $I_\lambda$ of the emission line of a single species is derived from the Boltzmann equation as:

$$I_\lambda = FC_i \frac{A_{ki} g_k}{Z_s(T)} e^{-\frac{E_k}{kT}}$$  \hspace{1cm} (3)

and,

$$\ln \frac{I_\lambda}{A_{ki} g_k} = -\frac{1}{kT} E_k + \ln \frac{C_i F}{Z_s(T)}$$  \hspace{1cm} (4)

where $A_{ki}$ is the transition probability, $g_k$ is the statistical weight for the upper level, $E_k$ is the excited level energy, $T$ is the temperature, $k$ is the Boltzmann constant, $Z_s(T)$ is the partition function of the species, $F$ is an experimental factor and $C_i$ is the species concentration. Table 1 shows spectroscopic parameters of the Si emission lines used to determine electronic temperature.
Table 1. Spectroscopic parameters of neutral Si (I) transition lines used to determine plasma temperature.

| Wavelength (nm) | $E_k$ (eV) | $A_{ki}$ | $g_k$ | $g_i$ |
|----------------|------------|----------|-------|-------|
| 250.69         | 4.9538     | 5.47E+07 | 5     | 3     |
| 253.24         | 6.8031     | 2.45E+07 | 3     | 1     |
| 263.13         | 6.6191     | 1.06E+08 | 3     | 1     |

Plotting the left hand side of Eq. (4) versus the excited level energy $E_k$, the plasma temperature can be obtained from the slope of obtained straight line (Fig. 4).

Figure 3. Spectral region used to determine Si/Al ratio.

Figure 4. Boltzmann plot for three lines of Si.
If we know the temperature of the plasma we can obtain $k_{t,\text{Si}}$ and $k_{t,\text{Al}}$ coefficients, ratio atomic densities may be deduced from the intensity ratios measured of the plasma emission. With this procedure we can check the stoichiometry of the sample. In this work we have calculated the $k_t$ coefficients for the emission the lines of Si (298.76 nm) and Al (308.22 nm) using spectral data provided by NIST databases [9]. The results obtained using the equation 1 show an intensity ratio $\text{Si}/\text{Al}=16.1$; that is according with $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of the zeolite studied here.

4. Conclusion

This work shows that the LIBS technique can be used to determine the composition of zeolites of very easy and quick.

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