

Sample: **ZnO/HAP (Reverse Micelle)**

Processing option: All elements analysed (Normalised)

| Spectrum | In stats | O | P | Ca | Zn |
|------------|----------|-------|-------|-------|-------|
| Spectrum 1 | Yes | 31.89 | 17.23 | 28.59 | 22.29 |
| Spectrum 2 | Yes | 18.63 | 23.52 | 43.45 | 14.40 |
| Spectrum 3 | Yes | 30.17 | 26.78 | 40.84 | 2.20 |
| Spectrum4 | Yes | 22.39 | 28.65 | 48.95 | 0.00 |
| Spectrum 5 | Yes | 17.02 | 15.32 | 24.77 | 42.89 |

All results in atomic%

| | | | | |
|----------------|-------|-------|-------|-------|
| Mean | 24.02 | 22.30 | 37.32 | 16.36 |
| Std. deviation | 6.72 | 5.84 | 10.24 | 17.40 |
| Max. | 31.89 | 28.65 | 48.95 | 42.89 |
| Min. | 17.02 | 15.32 | 24.77 | 0.00 |

Kinetic analysis

According Langmuir adsorption isotherm, the rate expression is:

$$\text{Rate} = k \frac{K [R]}{1 + K [R]} \quad (1)$$

Where K is the adsorption coefficient for cyclohexanol, k is the rate constant and $[R]$ is concentration of cyclohexanol.

According to Langmuir – Hinshelwood kinetic theory, the rate of reaction is:

$$\text{Rate} = k_r \theta_R \theta_{O_2} \quad (2)$$

Where k_r , θ_R and θ_{O_2} represent the rate constant and the fraction of surface covered by cyclohexanol and molecular oxygen respectively.

In the solvent-free conditions, due to the negligible change in the concentration of alcohol, θ_R can be taken equal to 1 and therefore, Eqn (2) changes to

$$\text{Rate} = k' \theta_{O_2} \quad (3)$$

At a constant oxygen pressure, Eqn (3) will become

$$\text{Rate} = k'' \quad (4)$$

Integration of Eqn (4) will change it to

$$(R)_t = -k'' t \quad (5)$$

Where $(R)_t$ is the amount of cyclohexanol left at time (t).

In addition to the Langmuir isotherm for adsorption of liquid alcohol on the surface of heterogeneous catalyst, there are the other isotherms in this area, Temkin or Freundlich adsorption isotherms. The rate expression for Temkin adsorption isotherm is given in Eqn (6) where in, where K_1 and K_2 are constants related to the heat of adsorption:

$$\text{Rate} = k_r (K_1 \ln K_2 [R]) \quad (6)$$

Considering the Freundlich adsorption isotherm, the rate of reaction is:

$$\text{Rate} = k_r K [R]^{\frac{1}{n}} \quad (7)$$

Where K is adsorption coefficient for alcohol and n is a constant.²⁸⁻³⁰

By applying equations (1) , (6) and (7) in the time profile data (Fig. 6) by using Curve Expert software, it has been found that Eqn (1) has best fit to experimental data and therefore Langmuir isotherm can be describe the adsorption of cyclohexanol on the surface of ZnO/HAP catalyst.