$ZnAl_2O_4$ powders prepared by combustion synthesis and their adsorbent properties

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1. Introduction

$ZnAl_2O_4$ (gahnite), is a normal spinel, which possesses valuable properties (hydrophobic behavior, low surface acidity, high thermo-mechanical resistance, high thermo-chemical stability, low sintering temperature, wide energy bandgap) used in a wide range of applications (Fig. 1).

- Adsorbtion, photocatalytic degradation of pollutants, catalyst and catalyst support
- Host matrix for ceramic pigments, NIR reflective pigments and phosphor materials
- Optical reflective coatings for aerospace applications and sensing applications

Fig. 1. Some of the most important applications of $ZnAl_2O_4$.

For many of these applications (e.g. adsorbent material), specific surface area represents a key parameter, which dictates the material behavior. Therefore tuning the preparation method in order to obtain large/low surface area $ZnAl_2O_4$ powders is one of the main priorities in the field.

2. Experimental

Raw materials: $Zn(C_2H_3O_2)_2{\cdot}2H_2O$ and CH_4N_2O (Merck), $Al(NO_3)_3{\cdot}9H_2O$ (Fluka), NH_4NO_3 (Reactivul), Methyl Orange - MO ($C_{14}H_{14}N_3NaO_3S$, λ_{MO} = 464 nm), Indigo carmine - IC ($C_{16}H_8N_2Na_2O_8S_2$, λ_{IC} = 610 nm), Methylene blue - MB ($C_{16}H_{18}ClN_3S$, λ_{MB} = 665 nm).

$$6\ Zn(C_2H_3O_2)_2{\cdot}2H_2O_{(c)} + 12\ Al(NO_3)_3{\cdot}9H_2O_{(c)} + 14\ CH_4N_2O_{(c)} + 48\ NH_4NO_{3(c)} = 6\ ZnAl_2O_{4(c)} + 38\ CO_{2(g)} + 190\ H_2O_{(g)} + 44\ N_{2(g)} + 6\ O_{2(g)} \quad (1)$$

$$6\ Zn(C_2H_3O_2)_2{\cdot}2H_2O_{(c)} + 12\ Al(NO_3)_3{\cdot}9H_2O_{(c)} + 28\ CH_4N_2O_{(c)} + 48\ NH_4NO_{3(c)} + 15\ O_{2(g)} = 6\ ZnAl_2O_{4(c)} + 52\ CO_{2(g)} + 218\ H_2O_{(g)} + 58\ N_{2(g)} \quad (2)$$

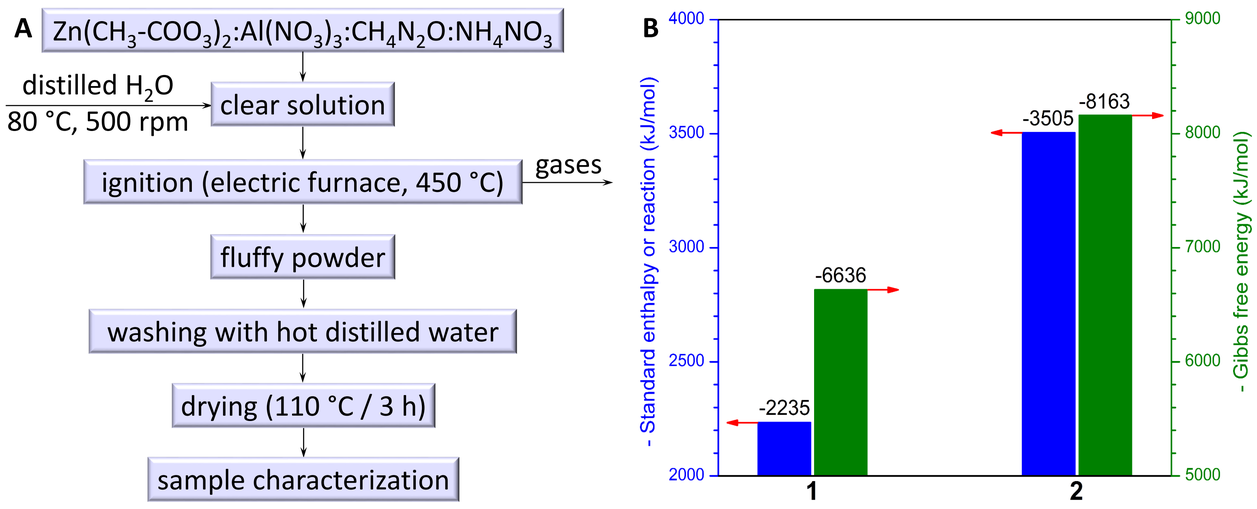

Fig. 2. Flowchart of $ZnAl_2O_4$ preparation (A). Standard enthalpy of reaction and Gibbs free energy (B).

Characterization techniques:

- **XRD**: Rigaku Ultima IV, CuKα, phase composition and crystallite size.
- **BET**: Micromeritics ASAP 2020, BET surface area, pore size and pore distribution.
- **Adsorption tests**: UVmini-1240 SHIMADZU, 25°C, 200 rpm, natural pH.

The amount of pollutant adsorbed, q_t (mg/g), was calculated according to Eq. (3) and the percentage of pollutant removed, R (%), was calculated by Eq. (4):

$$q_t = V(C_0-C_t)/m \quad (3) \qquad R = 100(C_0-C_e)/C_0 \quad (4)$$

where C_0, C_t and C_e (mg/L) are the concentrations of pollutant, initially, at any time t, and at equilibrium respectively, V the volume of solution (L) and m the mass of adsorbent (g).

3. Results and Discussion

Table 1. Characteristics of $ZnAl_2O_4$ samples prepared by solution combustion synthesis.

No.	T_{ad} (°C)	D_{XRD} (nm)	S_{BET} (m^2/g)	V_{BJH} (cm^3/g)	D_{pore} (nm)	R (%)		
						MO	IC	MB
1.	847	5	156	0.16	3.4	75.6	67.9	0.0
2.	1164	16	27	0.04	4.5	23.3	54.0	0.0

T_{ad} – adiabatic temperature, D_{XRD} – crystallite size, S_{BET} – specific surface area, V_{BJH} – pore volume, D_{pore} – pore diameter, R – removal efficiency

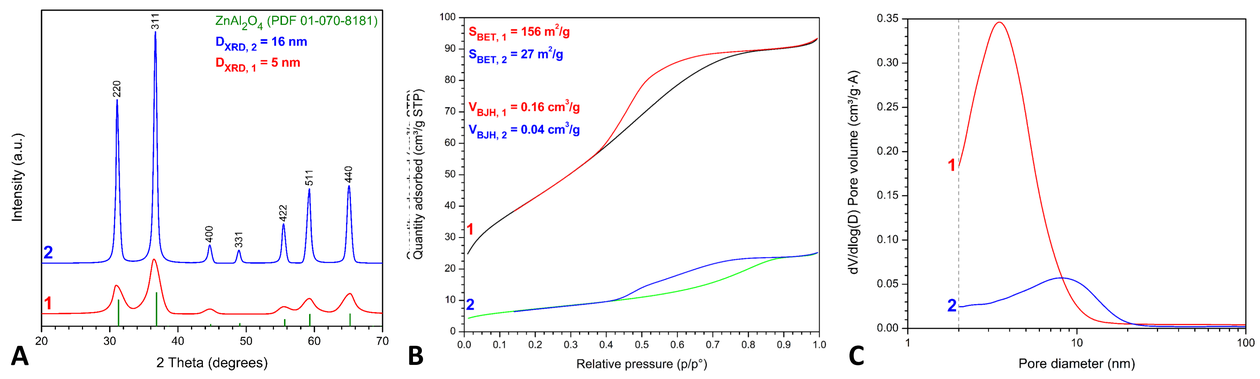

Fig. 3. XRD patterns (A), N_2 isotherms (B) and pore size distribution (C) of the prepared samples.

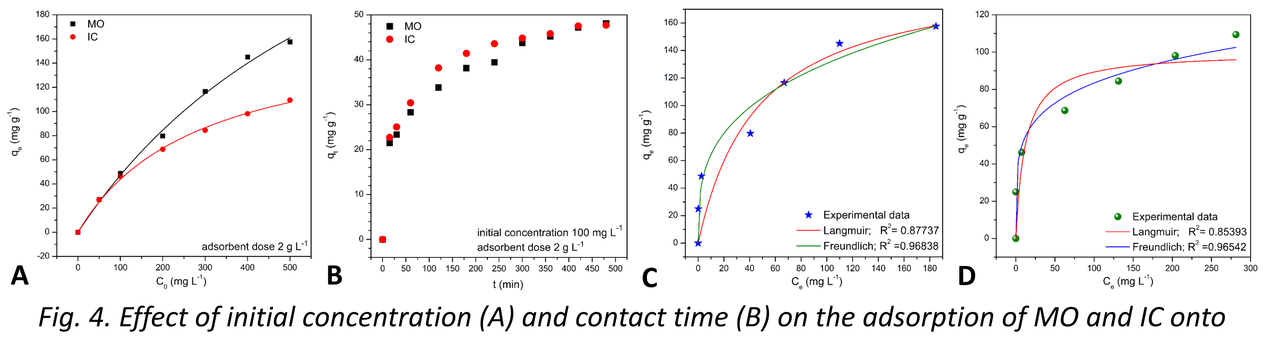

Fig. 4. Effect of initial concentration (A) and contact time (B) on the adsorption of MO and IC onto sample 1. Isotherm plots for the adsorption of MO (C) and IC (D) onto sample 1.

Table 3. Isotherm parameters (MO, IC / sample 1).

Isotherm model	Parameters	Pollutant	
		MO	IC
Langmuir	q_m (mg g^{-1})	197.65	100.02
	K_L (L mg^{-1})	0.0216	0.0835
	R^2	0.87737	0.85393
Freundlich	K_F (($(mg^{1-(1/n)}L^{1/n})g^{-1}$))	31.77	33.25
	n	3.257	5.006
	R^2	**0.96838**	**0.96542**

Table 4. Kinetic parameters (MO, IC / sample 1).

Kinetic model	Kinetic parameters	Pollutant	
		MO	IC
Pseudo-first-order, A	$q_{e,calc.}$ (mg g^{-1})	39.02	38.67719
	$q_{e,exp.}$ (mg g^{-1})	48.09	47.71748
	$k_1{\cdot}10^3$ (min^{-1})	7.85	7.32
	R^2	0.95137	0.97832
Pseudo-second-order, B	$q_{e,calc.}$ (mg g^{-1})	51.9	50.5
	$q_{e,exp.}$ (mg g^{-1})	48.09	47.71748
	$k_2{\cdot}10^4$ (g mg^{-1} min^{-1})	3.71	5.93
	R^2	**0.99259**	**0.99788**
Elovich, C	α (mg g^{-1} min^{-1})	3.2561	7.523414
	β (g mg^{-1})	0.1076	0.1261
	R^2	0.99221	0.98525
Intraparticle diffusion, D (second portion)	k_i (mg g^{-1} $min^{-0.5}$)	1.41069	0.9311
	c (mg g^{-1})	18.226	28.56662
	R^2	0.98463	0.97729

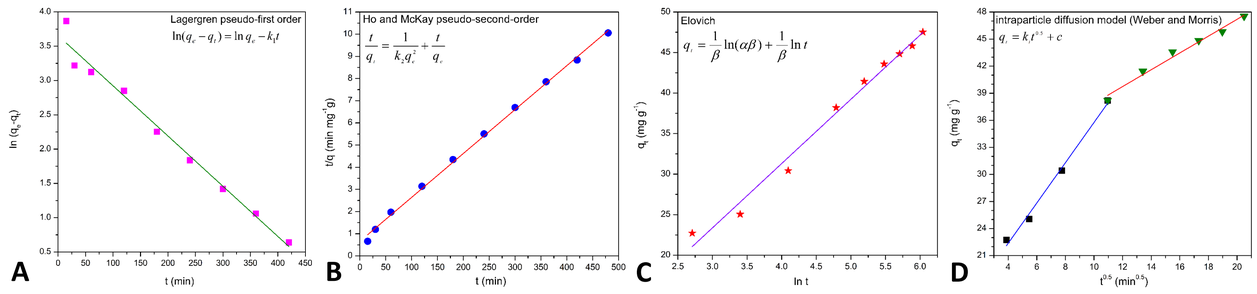

Fig. 5. Kinetic models fitting for the adsorption of IC onto sample 1.

4. Conclusions

- Metal nitrate/fuel ratio dictates the exothermicity of combustion reactions and therefore the properties of the resulted powder (surface area, adsorption capacity).
- Adsorption efficiency of Methyl Orange and Indigo Carmin is related to the electrostatic interactions between the positively charged surface of the adsorbent and the dye anions.
- The sorption kinetics of Methyl Orange and Indigo Carmin is well described by the pseudo second-order model.
- The equilibrium data of Methyl Orange and Indigo Carmin adsorption were correlated with Freundlich isotherm, indicating the heterogeneous nature of the adsorbent surface.
- The higher adsorption capacity for Methyl Orange as compared to Indigo Carmin may be explained by the smaller molecule of Methyl Orange.

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