

## Synthesis and Properties of Zinc Aluminate Catalyst

by J. Wrzyszc<sup>1</sup>, M. Zawadzki<sup>1</sup>, H. Grabowska<sup>1</sup>, W. Miśta<sup>1</sup> and J. Trawczyński<sup>2</sup>

<sup>1</sup>Institute of Low Temperature and Structure Research, Polish Academy of Sciences,  
50-950 Wrocław-2, P.O. Box 1410, Poland

<sup>2</sup>Institute of Chemistry and Technology of Petroleum and Coal, Wrocław University of Technology,  
50-344 Wrocław, Gdańska 7/9, Poland

(Received December 18th, 2000; revised manuscript January 17th, 2001)

Recently, the growing interest in ZnAl<sub>2</sub> 4 li ti t l t t l t i h . i l m o i t t h i g h h m o l t i l i t , h i g h h i l i t , i t t t t t i t t h m o t i t i l t l t i k i t l i t i . i l m o i t h t i - i t i h h i m o h l q i h l t i q t i , - i l l i m o i t i h 1 5 . t h h t t i t l t i h h i i q q t 6 q l h q t i t m o g - t l m o l i l q l i h t i l h l 7 . t i t i i q h q g t i l - 8 , i m o i t i l h 9 q i h m o h l t i h l 1 0 .

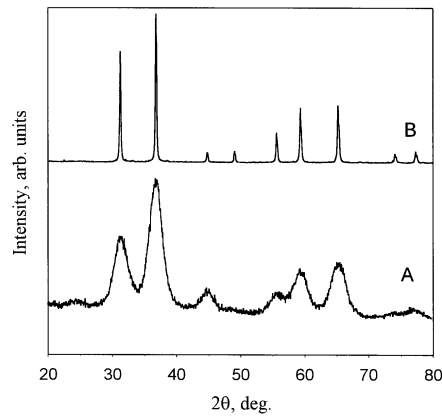
The purpose of this study was to characterize the ZnAl<sub>2</sub> 4 i l t i q i h - q h m o l q t m o i t t i t i t i t m o t i h m o l 6 8 l h l . D h q t i S q h q g t i l h l t l t h t q i q m o h . m o h m o t q t m o t q h q t i , i k i g i h l i h 1 1 1 4 , h h h m o i l q h q g t - i g t 1 5 2 0 . A h h t m o t i l h l l t h - t i h t h h t i t i h t l t m o t t t i t k i - t i . h i t q t i m o l l h l q k i q i t i i l m o i t .

The catalyst used for this study was prepared as follows: predetermined amounts of aluminium and zinc nitrates were dissolved in 2.5 dm<sup>3</sup> q i t i l l q t t m o t t . l q j t q t 8.8 q i g , i h t i g h q i q m o t m o o i l t i ( 2 5 t . % ) t h i t t l t i . h m o i t t i q 2 5 m o i . q h i i t t m o q i l t q q h q l t h i h q i t i l l q t . h t t , 4 q m o 3 t q q q t h k i q h t i q l h t q i t l i h t t t t i q 0.1 q i g 3 h . A t l i g h t l i k i t t m o t m o t , h t i q q t t h q q q q l l i g t i t h l t q t m o t . h l t i g g l t q q , i q i q q l i q t 8 7 3 4 h . h t i q t l t h q i t h 0.6 1.2 m o t i l . - - q q i t i t t t i q i h 2 0 - 3 q i t m o t i h i - i l t q q i t i . h t q q t m o t m o t m o 1 0 t 8 0 ( 2 )

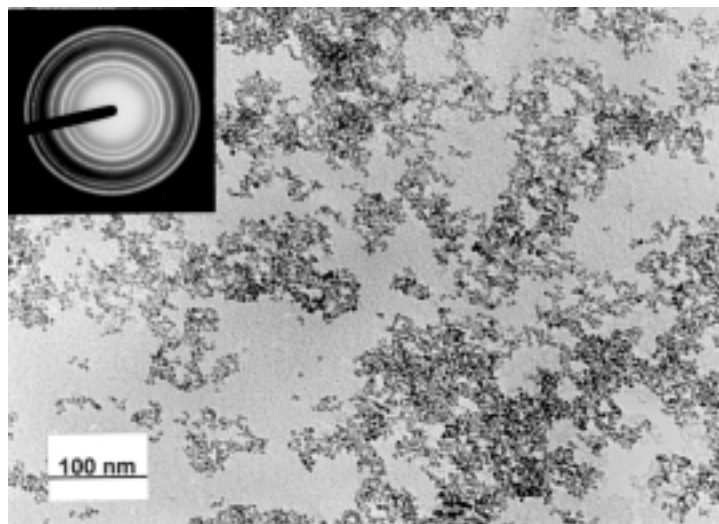
ih t 0.05 / S. h l tti m t l l t q i g h l t  
 itti g g n s S 21. h m o i t i h t l t  
 i q t i g h AB -500 t m o i i l t m o i i h l -  
 t i l t g 90 . h i i q h i q i t i t i  
 q t m o i q B t i q h D l i n e - h o h q , t i l , q  
 h i t g q t h t m o t S l i S i q - i t g t q q l m o t i  
 q , i g h t m o t i 1900 t . h q i t , i . e .  
 h t t i i B t q t h h t l t , -  
 t l i h q i g h t t q i q i h m o l l i -  
 q i h q q i q i 22 . i i t A l <sub>2</sub> 4 q t m o i q  
 m o q t i 2 23 25 . q i q q t i t l i h q q  
 h t m o t - g m o q q t i ( D ) 2 q q t m o t m o -  
 t . h D m o q i g h m o q l t , t l l q  
 m o t . h 100 m g m o l t t q i h l i n e ( 30 m o l m o i ) t 773 0.5 h  
 q q t 2 l 10 m o i t m o t m o t . l q q 2  
 m o q i g h l i n e h m o l t m o t m o t q t h t h  
 t m o t i q t 773 t h t 10 m o i . h 2 S t t i i  
 h l t m o q i g h i m o m o m o i t 200 q -  
 l m o t m o t .

The reactions of the transformation of the normal C<sub>6</sub>-C<sub>8</sub> l h l i q t  
 i g t i l i q q l t m o q m o h i i l t i -  
 l l h t q t i l t t i h i q i m o t 8 m o . A t l l  
 l t q h m o l l q h t m o t m o m o t l g h t l t  
 q . 3 m o <sup>3</sup> t l t q . h h l h l t q i q l i q t i -  
 S l m o h t h t m o i m o i h h l i q h l l i t  
 = 3.0 / t h ( l q 1.0 h <sup>1</sup> ) . m o t i q t t i l  
 t i i i g t m o t . A t h t t i i l i m o h q t i  
 - l t q t m o t , h m o t i q t c a 2 h . h  
 q q q t l q g h m o t g h . h h m o t g h  
 6890 q q i h D q t t q l m o - 5 ( 30 m o 0.32 m o i l l q  
 i h h h o h l i l i ) . l i n e q i g .

The X-ray powder diffraction patterns of the hydrothermally synthesized  
 ZnAl<sub>2</sub> 4 m o l , l i g h t m o t t m o t , h i g l . h  
 D t t m o l l i t q t 873 ( q . 1 A ) q m o t t q q , i q i -  
 t i g h i g h m o l q i i q i m o q h m o t i h q i q A l <sub>2</sub> 4  
 phase. h h q t t q . h q i t i h i l m o i t t -  
 l t m o m o i t q t h t m o t t t m o t ,  
 g i g t i l i h m o l . h m o l l i t q t 1273 h D t t  
 ( q . 1 B ) h i g l - h i i l t t i h l t t i t t l  
 i l m o i t . t l l i A l <sub>2</sub> 4 h g t l l i t i , m o q  
 - q i g l i h ( 311 ) l t i , i t 30 m o . h m o h l -  
 g h h q h m o l l t i q i l m o i t m o l q i q t 413 , i q  
 , i t q i g 2 , l i g h t h t i q A l <sub>2</sub> 4 i m o -



**Figure 1.** X-ray diffraction patterns of  $ZnAl_2O_4$  synthesized at 873 K (A) and at 1423 K (B).



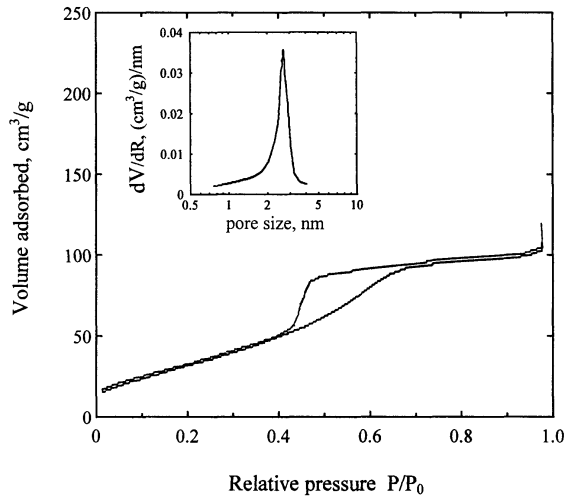
**Figure 2.** TEM micrograph of hydrothermally synthesized zinc aluminate sample dried at 413 K with SAED pattern showing rings that match d-spacings for the spinel structure of  $ZnAl_2O_4$ .

The XRD patterns of  $ZnAl_2O_4$  synthesized at 873 K (A) and at 1423 K (B) are shown in Figure 1. The pattern of the sample synthesized at 873 K shows broad peaks, indicating a poorly crystalline or amorphous structure. In contrast, the pattern of the sample synthesized at 1423 K shows sharp, well-defined peaks, indicating a highly crystalline structure. The sharp peaks in the high-temperature sample correspond to the spinel structure of  $ZnAl_2O_4$ .

**Table 1.** Properties of zinc aluminate catalyst after calcination at 873 K for 4 h.

Phase composition	ZnAl <sub>2-4</sub>
Al <sub>2-4</sub> (wt %)	8.0928 (0.0005)
Average crystallite size, nm	7
Surface area, m <sup>2</sup> /g	93
Porosity (τ/ρ = 0.95), m <sup>3</sup> /g	0.14
Mean pore radius, nm	2.8
Internal surface area, m <sup>2</sup> /g	195
External surface area, m <sup>2</sup> /g	0
Internal volume, cm <sup>3</sup> /g	180

The nitrogen adsorption-desorption isotherm of ZnAl<sub>2-4</sub> catalyst after calcination at 873 K for 4 h is shown in Figure 3. The isotherm exhibits a typical Type IV behavior with a hysteresis loop, indicating the presence of mesopores. The pore size distribution (PSD) curve, shown as an inset, shows a sharp peak at approximately 2.8 nm, which corresponds to the mean pore radius. The total surface area is 93 m<sup>2</sup>/g, and the internal surface area is 195 m<sup>2</sup>/g. The porosity is 0.14 m<sup>3</sup>/g, and the internal volume is 180 cm<sup>3</sup>/g.



**Figure 3.** Nitrogen adsorption isotherm collected at 77 K and pore size distribution for ZnAl<sub>2-4</sub> catalyst. The inset shows the pore size distribution (PSD) curve, which is a derivative of the pore volume with respect to the pore diameter of the adsorbent.

Alcohol	Temperature K	Conversion %	Liquid products composition, %					Σ h
			alkene	aldehyde	ether	ester	ketone	
n-h l	573	21.1	traces	4.2	—	13.3	0.3	3.3
	603	37.2	0.7	9.9	—	23.7	0.7	2.2
	633	67.9	1.2	23.5	1.2	38.9	0.8	2.3
	663	92.3	2.4	34.6	5.8	37.1	2.6	9.8
	688	95.6	4.8	28.6	11.8	17.0	13.0	20.4
n-h t l	573	23.6	0.7	4.4	—	16.0	1.2	1.3
	608	49.0	1.4	14.1	traces	30.5	1.7	1.3
	638	77.7	4.5	34.9	0.6	33.0	2.3	2.4
	668	94.3	5.5	34.1	2.2	30.0	12.3	10.2
	698	97.1	12.0	23.9	10.0	2.2	25.7	23.3
n- t l	573	25.8	—	3.6	—	17.3	—	3.9
	608	45.9	1.9	10.3	—	26.9	traces	6.8
	638	67.6	2.8	27.4	0.5	30.5	0.4	6.0
	668	92.7	5.8	37.0	3.2	29.8	3.7	13.2
	693	97.2	10.4	28.0	7.5	5.9	12.3	33.1

Zinc aluminate, which was hydrothermally synthesised according to the applied procedure, showed both acidic and basic natures, thus it should exhibit both dehydration and dehydrogenation activities. Transformations of normal C<sub>6-8</sub> l h l t i q q h l t n o i q i l 2, h i h t h q q h i l h l t t q h i q h n o i l i q q t. i n o i t h t t i t n o t i n o l l h l. h t i t l t 573 698. D i g h l h l i, q- t q h q g t i q q t i q i h t i q t. D h q g t i l q t q t i g i i t n o t i t q- h q : t 34.6% n-h l t 663, 34.9% n-h t l t 638 q 37.0% n- t l t 668 n-h l, h t l q t l, t i l. h t t h t i q q h q q t t i t q n o t i l t. h q h q g t i h l h l n o i l i t q h q t i t q i g l i q h. h t i t l h l Al<sub>2</sub> 4 i q i t n o h t - q h i q t l t, h i g i t i, h i h i g - h i i h q h q g t i l h l 17. h i g g t h t h t n o t i n o l l h l Al<sub>2</sub> 4 t l t q q t g l i t q- t i. h t i t q i q i n o q h t h i n o i t t l t q n o t t h q i q i t i.

## Acknowledgment

The research was performed under financial support from the Polish State Committee for Scientific Research under grant no. 3 T09B 063 16.

## REFERENCES

1. Le Peltier F., Chaumette P., Saussey J., Bettahar M.M. and Lavalley J.C., *J. Mol. Catal. A: Chem.*, **122**, 131 (1997).
2. Chaumette P., Coutry Ph., Barbier J., Fortin T., Lavalley J.C., Chauvin C., Kinnemann A., Idriss H., Sneed R.P.A. and Denise B., in: Proceedings 9<sup>th</sup> International Congress on Catalysis, Eds. M.J. Philips, M. Ternan, The Chemical Institute of Canada, Calgary, 1988, p. 585.
3. Kinnemann A., Idriss H., Hindermann J.P., Lavalley J.C., Vallet A., Chaumette P. and Coutry Ph., *Appl. Catal.*, **59**, 165 (1990).
4. Bart J.C.J. and Sneed R.P.A., *Catal. Today*, **2**, 1 (1987).
5. Kienle C., Schnizer C., Lentmaier J., Schaal O. and KemmlerSack S., *Mater. Chem. Phys.*, **49**, 211 (1997).
6. Roesky R., Weigury J., Bestgen H. and Dingerdissen U., *Appl. Catal. A: General*, **176**, 213 (1999).
7. Stern R., Hillion G., Rouxel J.-J. and Leporq S., US Pat. 5908946; 1999.
8. Valenzuela M.A., Aguilar G., Bosch P., Armendariz H., Salas P. and Montoya A., *Catal. Lett.*, **15**, 179 (1992).
9. Wrzyszczyk J., Zawadzki M., Trawczyński J., Grabowska H. and Mišta W., *Appl. Catal. A: General*, (in press).
10. Grabowska H., Mišta W., Trawczyński J., Wrzyszczyk J. and Zawadzki M., *Res. Chem. Intermed.*, (in press).
11. Lundeen A.J. and Van Hoozer R., *J. Org. Chem.*, **32**, 3386 (1967).
12. Niiyama H. and Echigoya E., *Bull. Chem. Soc. Jpn.*, **44**, 1739 (1971).
13. Canesson P. and Blanchard M., *J. Catal.*, **42**, 205 (1976).
14. Vohs J.M. and Barteau M.A., *Surface Science*, **221**, 590 (1989).
15. Komarevsky V.J. and Coley J.R., *J. Am. Chem. Soc.*, **63**, 700 (1941).
16. Di Cosimo J.L., Diez V.K., Xu M., Iglesia E. and Apestegnia C.R., *J. Catal.*, **178**, 499 (1998).
17. Wrzyszczyk J., Grabowska H., Klimkiewicz R. and Syper L., *Catal. Lett.*, **54**, 55 (1998).
18. Wang Y.G. and Davis B.H., *Appl. Catal. A: General*, **180**, 277 (1999).
19. Hashimoto K. and Toukai N., *J. Mol. Catal. A: Chem.*, **145**, 273 (1999).
20. Kamimura Y., Sato S., Takahashi R., Sodesawa T. and Fukui M., *Chem. Lett.*, **232** (2000).
21. Łasocha W. and Lewiński K., *J. Appl. Cryst.*, **27**, 437 (1994).
22. Kung H.H., in: Studies in Surface Science and Catalysis, vol. 45, Eds. B. Delmon, J.T. Yates, Elsevier, Amsterdam-Oxford-NY-Tokyo, 1989, p. 80.
23. Hattori H., *Chem. Rev.*, **95**, 537 (1995).
24. Di Cosimo J.L., Apestegnia C.R., Ginés M.J.L. and Iglesia E., *J. Catal.*, **190**, 261 (2000).
25. Hashimoto K. and Toukai N., *J. Mol. Catal. A: Chem.*, **145**, 273 (1999).
26. Zawadzki M. and Wrzyszczyk J., *Mater. Res. Bull.*, **35**, 109 (2000).
27. IUPAC, *Pure Appl. Chem.*, **57**, 603 (1985).