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Synthesis and Characterization of Structural, Textural and Catalytic Properties of Several AB_2O_4 (A = Zn^{2+} (Cu^{2+}); B = Al^{3+}, Cr^{3+}) Nanospinels*

Nguyen Hong Vinh,† Le Thanh Son, Nguyen Thanh Binh, Tran Thi Nhu Mai, Dang Van Long, Nguyen Thi Minh Thu, Vo Thi My Nga, and Hoa Huu Thu
Department of Petroleum Chemistry, Faculty of Chemistry, Hanoi University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam
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In this report, several series of AB_2O_4 (A = Zn^{2+} (Cu^{2+}); B = Al^{3+}, Cr^{3+}) nanospinels were synthesized by hydrothermal method at different hydrothermal temperatures in autoclave. In this synthesis, the thermodifferential analysis method was used to find out the optimum temperature of calcinations for nanospinel phase formation. The structural, textural properties of the catalysts as-obtained were characterized by physical methods: DTA-TGA, XRD, TEM, BET. Their catalytic activity was measured by using oxidative dehydrogenation reaction of ethylbenzene to styrene at different temperatures. From experiment results obtained, it is observed that in the presence of the nanospinels catalysts, the catalytic activity and selectivity in styrene is high.
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I. INTRODUCTION

Styrene is produced industrially ca. 17 million tons by year in the world by dehydrogenation of ethylbenzene over iron oxide bulk catalysts promoted by potassium metal ions [1]. Their activity catalytic decreases slowly with usage because of the potassium ions migrated from the surface to the bulk. Spinel oxides, having cation distribution at two crystallographic environments, are reported to have more activity for ethylbenzene dehydrogenation [2]. There are many works investigated the active surface of normal spinel oxides [3–5]. They showed also that the bulk spinel catalysts exhibiting the specific surface area small and that the activity of bulk spinels is significantly varied with respect to cations at the octahedral sites in hard conditions during dehydrogenation of ethylbenzene (temperature as high as 823-973 K; reductive atmosphere of hydrogen, etc.). In addition, ethylbenzene dehydrogenation reaction is a reverse one endothermal. That is why in the recent years, a lot of works has been reported by many investigators on new spinel materials that can catalysize dehydrogenation reaction of ethylbenzene to styrene [6–9] but nanospinel material used to be catalyst for ethylbenzene dehydrogenation are little [10]. Generally, the development of novel materials is a fundamental focal point of chemical research, and in particular, it is also nanoparticle formation research in recent decades and using nonoparticles as catalysts for chemical conversions. This interest is mandated by advancements in all areas of science, industry and technology. Up to now, several methods such as solid-state thermal reaction, hydrothermal, coprecipitation, and combustion [5–7] have been adopted for the synthesis of spinel nanoparticles using for many different aims.

In this paper, we reported at first, the synthesis of several nanospinels AB_2O_4 (A = Zn^{2+} (Cu^{2+}); B = Al^{3+} and Cr^{3+}) by the hydrothermal processing at optimum conditions determined by TG/DTA analysis (this means that the optimum temperature for the nanospinel phase formation the precursor sample are searched by the analysis). And then the structural and textural properties of the synthesized products are characterized by X-ray diffraction. The morphology and the particle size of the synthesized powder is analyzed by transmission electron microscope (TEM). Finally, the catalytic activity of the nanospinel materials is tested by ethylbenzene oxidative dehydrogenation to styrene in flow bed system of heterogeneous phase. The liquid products are analyzed by GC-MS.

II. EXPERIMENTAL

The normal AB_2O_4 (A = Zn^{2+} (Cu^{2+}); B = Al^{3+} and Cr^{3+}) spinel nanoparticles were prepared by hydrothermal processing. The analytic pure grade $Zn(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$ and NH_4OH were used as staring materials in the stoichiometric amounts for nanospinel formation desirable. The stoichiometric amounts of starting materials were made into a homogeneous solution in distilled water, and then adding in the solution of the metallic ions, the solution of 5wt% NH_4OH in stirring until pH = 7. The gel resultant was heated at 80°C for 1 hour, and this gel was transported in an autoclave and brought to 150-200°C for 24 hours. Taking a part of the gel obtained in this way, the thermodifferential analysis was done to find out the temperature for nanospinel formation. This temperature condition was verified by XRD analysis.

Thermal analysis of the precursor was realized by using a TG/DTG and DSC thermal analyzer (MODEL LABSYS 1600, FRANCE) at a heating rate of 10°C/min under air atmosphere to find out the nanospinel phase formation or complete crystallization temperature of the precursors.

X-ray diffraction measurements were made from JEOL

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†Corresponding author: nguyenhongvinh55@yahoo.com.vn

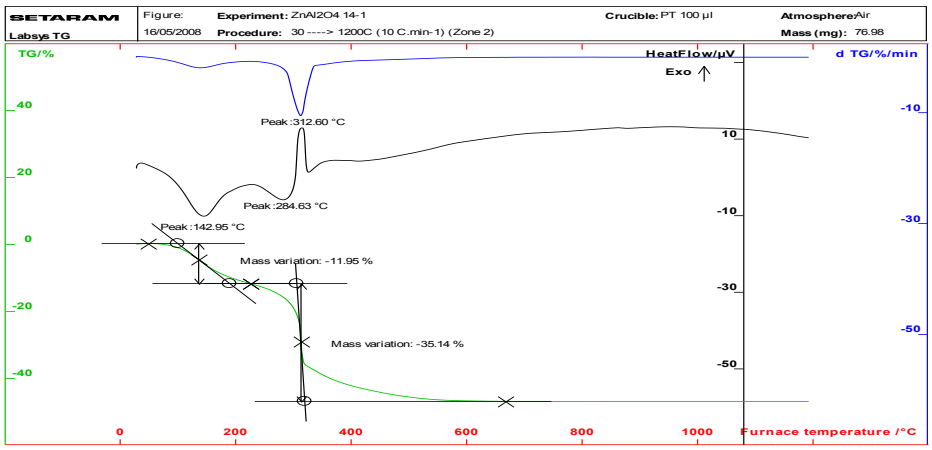

FIG. 1: TG, DTG, and DSC curves for the gel $Zn(OH)_2{\cdot}Al(OH)_3$ after aging in the autoclave at the temperature of 150°C for 24 h.

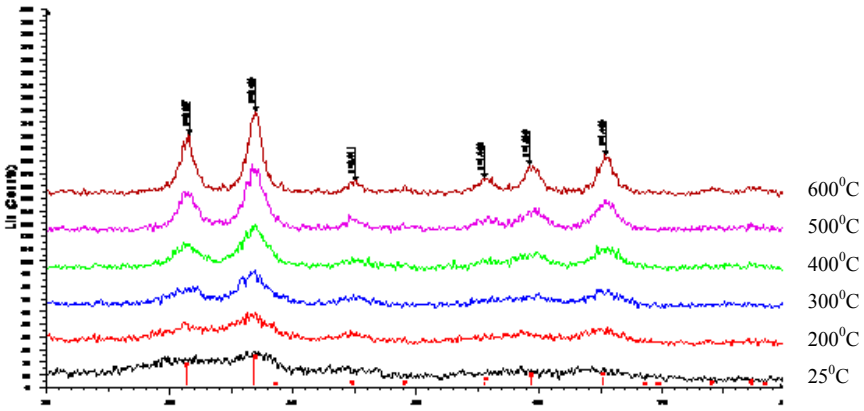

FIG. 2: XRD patterns of $ZnAl_2O_4$ particle sample.

X-ray diffractometer (Model: D8 5005 Advance, Brucker, Germany), using Cu-Kα radiation to identify the phase purity and structure conformity of the solid products obtained: AB_2O_4 (A = Zn^{2+} (Cu^{2+}); B = Al^{3+} and Cr^{3+}). The diffraction patterns were taken at 25°C in the range of $5° < 2\theta < 70°$. The scan rate was 2°/min.

The morphology of the nanospinels AB_2O_4 as obtained were analyzed by JEOL transmission electron microscope, model JEM 1010, operated at 200 KV.

In order to estimate a parameter characterizing the nanoparticle materials in heterogeneous catalysis, the nitrogen adsorption-desorption at 77 K were determined volumetrically using BET method on analyzer Micromeristics ASAP 2010. Before the experiment the adsorbents were outgassed at 493 K, $p \sim 10^{-2}$ Pa. The adsorption data were used to evaluate the BET specific surface area from the linear BET plots.

The evaluation of the catalytic activity of the nanospinels obtained in oxidative dehydrogenation reaction of ethylbenzene to styrene was made in flow bed system. The reaction is carried out by passing 10 ml of the air/min along with ethylbenzene in the temperature range of 400-500°C. The liquid products are analyzed by GC-MS (Model HDGC 6890-HPMS 5973, USA). All analytical measurements were made after a steady activity level was established.

III. RESULTS AND DISCUSSIONS

A. Characterization

The TG, DTG and DSC thermograms obtained for the parent mixture are shown in Fig. 1. From the DSC (100-1000°C) curve, two endothermic effects (located in the temperature ranges 143°C and 265°C) and one exothermic effect (located at 312.6°C) can be distinguished.

The first endothermic effect can be attributed to the dehydration of the aluminum hydroxide intermediate. The second endothermic peak, which is maximum at ~265°C can be assigned to $Zn(OH)_2 \rightarrow$ZnO transformation. The sharp exothermic peak observed at 312.6°C is attributed to the formation of the bond Zn–O–Al of the nanospinel material.

To ensure that the spinel or any other phase has been formed, the samples calcinated at 200-700°C for 5 h were registered the X-ray diffraction patterns. The results are presented in Fig. 2.

XRD results of the samples calcinated at different tem-

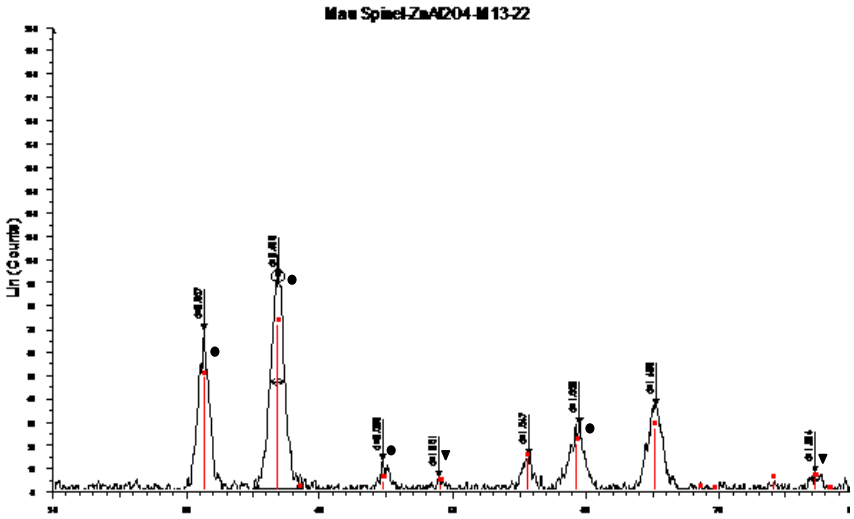

FIG. 3: XRD pattern of $ZnAl_2O_4$ particle sample calcinated at 600°C for 5 h. Symbols (•) and (▽) represent $ZnAl_2O_4$ and Al_2O_3, respective.

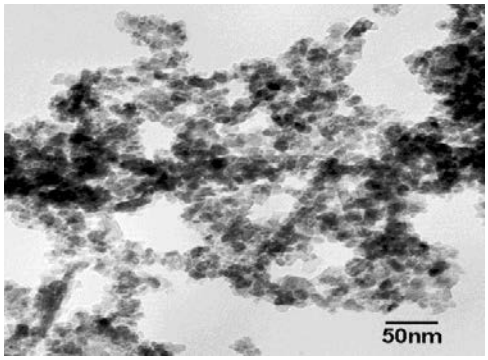

FIG. 4: TEM image of $ZnAl_2O_4$ spinel nanoparticle calcinated at 600°C.

peratures showed that $ZnAl_2O_4$ spinel- type formed when the gel obtained after aging in the autoclave for 5 h was calcinated at temperatures higher than 300°C, but several weak diffraction peaks of Al_2O_3 phase were also observed in the pattern especially at 600°C (Fig. 3).

The crystallite size calculated according to Scherrer's equation was about 4-5 nm. When the calcination was passed 600°C, it is observed the sintering of the material. This confirms that the synthesis method of Al_2O_4 (A=Zn^{2+} (Cu^{2+}); B=Al^{3+}, Cr^{3+}) nanospinels can be made at the calcination temperature of 600°C.

Comparated to other synthesis methods of $ZnAl_2O_4$, the method used here was a high yielding and low-cost procedure. The inorganic precursor employed was $Zn(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$ and NH_4OH instead of the organo-metallic precursors. Water, the only solvent, replaced the environmentally unfriendly surfactants.

TEM image of $ZnAl_2O_4$ obtained in the calcinations temperature of 600°C is represented in Fig. 4. The TEM result showed the particle size is about 4-5 nm in agreement with the result obtained from calculation according to Scherrers' equation basing on it's XRD pattern.

TABLE I: Variation of ethylbenzene conversion (%) and selectivity in styrene (%) in the presence of $ZnAl_2O_4$ spinel nanomaterial at different reaction temperatures.

Reaction temperature (°C)	Ethylbenzene conversion (%)	Selectivity in styrene (%)
400	11.15	73.14
450	31.34	67.45
500	16.24	80.03

In order to research the catalytic possibility modified of the parent $ZnAl_2O_4$ spinel nanoparticles, $Zn_{0.5}Cu_{0.5}Al_2O_4$ (a part of moles of Zn^{2+} replaced by Cu^{2+}in tetragonal positions) spinel and $ZnCr_2O_4$ (Al^{3+} replaced by Cr^{3-} in octagonal positions in spinels structure) are synthesized by the same method. The XRD patterns of two samples are represented in Fig. 5.

These XRD patterns have showed that the spinel crystals were formed. Their TEM images are presented in Fig. 6.

It shows that the particles are composed of ultrafine particles with relatively uniform distributed size ca. 4-6 nm. No doubt, such nano size particles would facilitate the diffusion of the reagents to arrive the surface sites of the catalysts. So, an important parameter of the heterogeneous catalysts is its specific surface area.

The specific surface area of the $ZnAl_2O_4$ spinel nanoparticle is determined to be 75.035 m^2/g. According to Ref. [2], the bulk spinels present generally a specific surface area of ca. 10 m^2/g. The very high specific surface firms nano-particle size of this synthesized spinel $ZnAl_2O_4$.

B. Catalytic characterization

In this report, in order to investigate the influence of the metallic ions at the different positions in the normal

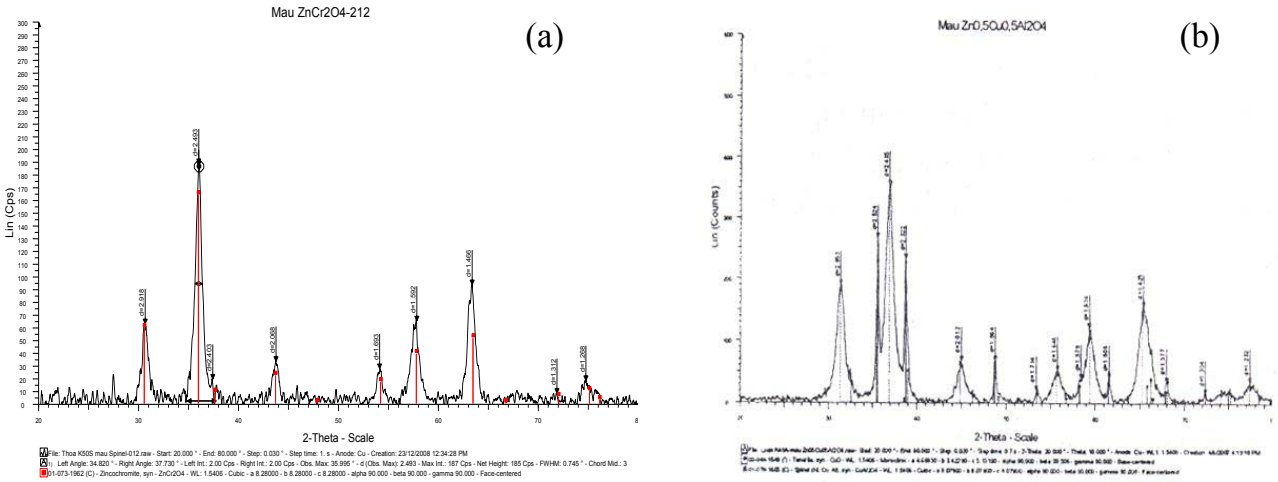

FIG. 5: XRD patterns (a) spinel $ZnCr_2O_4$ and (b) of spinel $Zn_{0.5}Cu_{0.5}Al_2O_4$. **Letters below the graphs are difficult to read. Can we delete these letters? Or could you provide us better figure?**

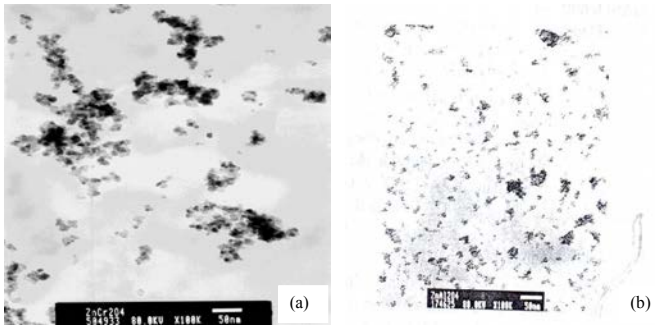

FIG. 6: TEM photograph of (a) $ZnCr_2O_4$ spinel particle and (b) $Zn_{0.5}Cu_{0.5}Al_2O_4$ spinel particle.

TABLE II: Variation of ethylbenzene conversion (%) and selectivity in styrene (%) in the presence of $ZnCr_2O_4$ spinel nanomaterial at different reaction temperatures.

Reaction temperature (°C)	Ethylbenzene conversion (%)	Selectivity in styrene (%)
300	28.54	35.17
350	36.30	78.14
400	29.22	14.78

TABLE III: Variation of ethylbenzene conversion (%) and selectivity in styrene (%) in the presence of $Zn_xCu_{1-x}Ai_2O_4$ spinel nanomaterial at reaction temperature of 400°C.

Catalysts	Ethylbenzene conversion (%)	Selectivity in styrene (%)
$ZnAl_2O_4$	11.15	73.14
$Zn_{0.5}Cu_{0.5}Al_2O_4$	24.71	78.26
$CuAl_2O_4$	34.44	82.79

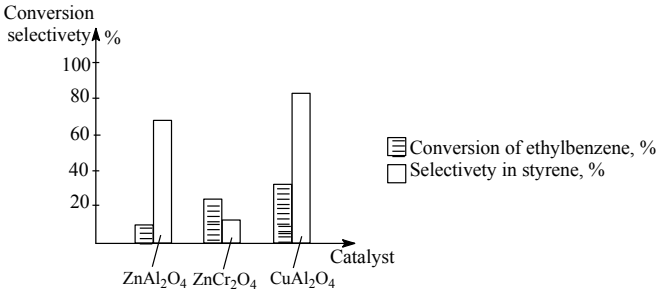

FIG. 7: Effect of the metallic cations in different positions in the $ZnAl_2O_4$ spinel nanostructure on ethylbenzene conversion and selectivity in styrene at reaction temperature of 400°C.

spinel structure on their catalytic activity in the oxidative dehydrogenation of ethylbenzene to styrene, the measurements of catalytic activity made in different operation conditions. The experiment results are represented in Tables I, II, and III.

The ethylbenzene oxidative dehydrogenation reactions to Styrene are realized in the temperature ranges much lower than the reaction temperatures under that the ethylbenzene oxidative dehydrogenation reaction to Styrene are made in presence of bulk spinel catalysts (generally, 600-700°C) [2], but these nanomaterials still exhibit their catalytic action even at the reaction temperature very low, 300°C with the conversion of 28.54% and the selectivity in styrene of 35.17% for $ZnCr_2O_4$ catalyst. This result supports the observations discussed above, our catalyst materials being nanospinels. From the results represented in Tables I and II, it was observed that the Cr^{3+} ions replace the octagonal positions of the ions Al^{3+} in the structure of spinel normal increased the conversion of ethylbenzene but the selectivity in styrene very low. Table III showed when the replacement of Zn^{2+} ions in the tetragonal positions by Cu^{2+} ions increased in the same time the ethylbenzene conversion and the styrene selectivity. For comparison, the results of Tables I, II, and III are presented in Fig. 7.

We suppose that the active site in the Cu-substituted

nanospinel catalyst is related with the structure of nanospinel phase. And this is the key parameter for catalytic activity of AB_2O_4 (A = Zn^{2+}, (Cu^{2+}); B = Al^{3+}, Cr^{3+}) spinels.

IV. CONCLUSION

The hydrothermal method is found to be an effective one in economy as well as environment for the synthesis of normal spinel AB_2O_4 (A = Zn^{2+}, (Cu^{2+}); B = Al^{3+}, Cr^{3+}) nanoparticles. These nanospinel catalysts have shown high catalytic activity and selectivity in ethylbenzene oxidative dehydrogenation to styrene in the range of low reaction temperature, ca. 400°C. The ethylbenzene conversion and the styrene selectivity is influenced by nature of metallic cations in the tetragonal and octagonal positions of nanospinel structure. Cu-substituted nanospinel catalyst showed the highest ethylbenzene conversion and selectivity in styrene in ethylbenzene oxidative dehydrogenation in operation conditions very soft.

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