

CHAPTER II

LITERATURE REVIEWS

Oxidative dehydrogenation (ODH), kinds of exothermic reaction, is the oxidation of alkane with oxygen to convert alkane into unsaturated hydrocarbon (alkene or diene) and water, which are the main products.

2.1 Catalysts in the oxidative dehydrogenation reaction

Zhou R. et al. [6] studied the effect of rare earth (Y, La, Ce) oxides on hexagonal mesoporous silicas (HMS) silica supported vanadia catalysts for the oxidative dehydrogenation of propane. The doping of Y, La oxides into the V-HMS catalyst affords a significant promotion in the selectivity to propylene while the Ce oxide exhibits a reverse effect for the oxidative dehydrogenation process. The characterization results show that the doping of rare earth oxides results in a significant modification of the redox and acid properties of the V-HMS catalysts. In addition, the formation of a new active phase of rare earth orthovanadates over the modified V-HMS catalysts was also identified. The correlation between the structural changes and the selectivity of the catalysts implied that the formation of new active phase of LaVO_4 and YVO_4 might be responsible for the improved catalytic performance.

The addition of La, Y oxides into the V-HMS catalyst allows a significant promotion in the selectivity to propylene, while the Ce oxide shows a reverse effect in the oxidative dehydrogenation of propane. The introduction of yttrium and lanthanum oxides results in a significant modification of the structural properties as well as of the redox and acid properties of the V-HMS catalysts. The formation of new active surface phases of Y and La-orthovanadates over the modified V-HMS catalysts was considered to be responsible for the improved catalytic performance of the rare earth doped catalysts. Our results clearly show that the rare earth oxides can be promising promoters for the vanadia catalyst system in the oxidative dehydrogenation of propane to propylene.

The oxidative dehydrogenation (ODH) of propane was investigated on vanadia dispersed on alumina containing a nominal polymolybdate monolayer. Dehydrogenation rates and selectivity on these catalysts were compared with those on vanadia domains dispersed on alumina. At a given vanadia surface density, ODH reaction rates per gram of catalyst were about 1.5–2 times greater on MoO_x -coated Al_2O_3 than on pure Al_2O_3 supports. The higher activity of vanadia dispersed on MoO_x coated Al_2O_3 reflects the greater reducibility of VO_x species as a result of the replacement of V–O–Al with V–O–Mo bonds. The MoO_x interlayer also increased the alkene selectivity by inhibiting propane and propylene combustion rates relative to ODH rates. This appears to reflect a smaller number of unselective V_2O_5 clusters when alkoxide precursors are used to disperse vanadia on $\text{MoO}_x/\text{Al}_2\text{O}_3$ as compared to the use of metavanadate precursor to disperse vanadia on pure Al_2O_3 . At 613 K, the ratio of rate coefficients for propane combustion and propane ODH was three times smaller on $\text{MoO}_x/\text{Al}_2\text{O}_3$ than on Al_2O_3 supports. The ratio of rate constants for propylene combustion and propane ODH decreased by a similar factor.

The dispersion of VO_x on alumina containing a monolayer equivalent of molybdena increases the catalyst activity (per V atom) and selectivity for propane ODH to propylene. The higher activity is ascribed to the formation of V–O–Mo bonds between the dispersed vanadia and the molybdena layer. The formation of these bonds appears to be facilitated by the use of vanadyl isopropoxide as the precursor for the dispersed vanadia. Analysis of the reaction kinetics shows that the ratios of the rate coefficients for propane and propylene combustion relative to propane ODH are significantly lower for vanadia supported on a monolayer of molybdena on alumina than those for vanadia supported on alumina alone. These results are unexpected and may be attributable to the presence of V–O–Mo bonds formed by reaction of the dispersed vanadia with the molybdena layer deposited on the alumina support. It is possible that these bonds are associated with the formation of polymolybdovanadate species [7].

Oxidative dehydrogenation of propane has been studied on $\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{MoO}_3/\text{TiO}_2$ catalysts, consisting of 1 and 5 monolayers of the deposited oxides, promoted with Li, K and Rb cations. Addition of alkaline cations: Li, K and Rb to $\text{V}_2\text{O}_5/\text{TiO}_2$ (VTi) and $\text{MoO}_3/\text{TiO}_2$ (MoTi) catalysts of low (a monolayer) and high (5

monolayer) content of the deposited oxides modifies their catalytic performance in oxidative dehydrogenation of propane, and acid-base properties studied by the probe reaction of isopropanol decomposition. For both types of catalysts and for low and high content of vanadium and molybdenum the total activity in oxidative dehydrogenation of propane decreases in the sequence: $V(\text{Mo})\text{Ti} > 1V(\text{Mo})\text{TiLi} > 1V(\text{Mo})\text{TiK} > 1V(\text{Mo})\text{TiRb}$. The selectivities to propylene at iso-conversion of propane increase in the same order. The acidity of the catalysts decreases and the basicity increases following the above sequence. The decrease in the activity may be due to blocking of the propane activation centers, the extent of this effect increasing with the increasing radius of the alkaline cations. The increase in the selectivity to propylene in oxidative dehydrogenation of propane may be due, on the other hand, to the increase in basicity and decrease in acidity of the promoted catalysts, which follow the order of decreasing electronegativity of the alkaline promoters. These changes in acidic-basic properties facilitate desorption of propylene, preventing its further oxidation on the surface to CO_x . Higher selectivities to propylene are observed on alkali promoted MoTi catalysts than on the VTi system and on high loading catalysts (both VTi and MoTi) as compared with monolayer preparations. The yields of propylene obtained (10-12%) show that potassium- and rubidium promoted vanadia-titania and molybdena-titania systems could be promising catalysts for oxidative dehydrogenation of propane. The addition of alkaline cations also modifies the dispersion of the deposited oxides, decreasing the amount of crystalline V_2O_5 and MoO_3 in the promoted catalysts [8].

The oxidative dehydrogenation of propane (ODHP) was studied over an optimized V-Mg-O catalyst at 500°C using the vacuum transient kinetic technique in the temporal-analysis-of-products (TAP) reactor. Partial and deep oxidation of propane occur at the same surface site but involve different forms of reactive oxygen, associated to different site arrangements: nucleophilic lattice oxygen takes part in the propane partial oxidation to propylene, while adsorbed electrophilic oxygen adspecies, originating from the gas-phase oxygen, are involved in the direct deep oxidation process of propane. The secondary oxidation of propylene could involve both types of oxygen species. In the absence of gas-phase oxygen, the oxidation state of the catalyst determines the importance of the consecutive propylene total oxidation.

The ODHP reaction mechanism was studied over an optimized V-Mg-O catalyst by use of the TAP reactor. A Mars-van Krevelen reaction mechanism was proposed involving a fast oxygen migration through the oxide lattice. However, oxygen labeling showed no gaseous oxygen exchange, revealing that oxygen could only be consumed irreversibly by the solid (reoxidation, creation of activated oxygen species) but not reversibly dissociated (like on a metallic surface). As far as oxygen species are concerned, lattice oxygen would be involved in the formation of propylene, while activated oxygen adspecies seemed to be related to the non-selective propane-to-Cox pathway. Indeed vanadium ions in various oxidation states and anionic vacancies have also to be considered to fully characterize the active sites. The following mechanistic scheme was tentatively proposed: a unique active site is considered with three possible states: oxidized (x_O), reduced (x) and superoxidised (x_{OO}); the selective route leading to propylene formation occurs on the oxidized site (x_O) a primary non-selective route oxidizing propane into CO_x involves the superoxidised sites (x_{OO}); a secondary non-selective route oxidizing propylene into CO_x also occurs in competition with the selective activation of propane; and gaseous oxygen would either regenerate the reduced active sites or react with them to form non-selective adspecies (x_{OO}) [9].

The oxidative dehydrogenation of propane with nickel molybdate catalysts has been kinetically studied, and the lattice oxygen appears to play a determinant role in propylene selectivity. With the aim of confirming this catalytic behaviour, a periodic-flow apparatus has been specifically designed for the reaction of propane with the lattice oxygen. With a conversion less than 2% only 1% of the oxygen of the monolayer is consumed, and the reaction is controlled by monolayer oxygen diffusion within the catalyst. The periodic system operates under stationary conditions, with high propylene selectivity. The catalyst deactivation takes place when metallic Ni is irreversibly formed on the catalyst surface [10].

The structure of vanadia dispersed on zirconia is strongly dependent on the surface density of vanadia and the temperature at which the deposited vanadia has been calcined. Small vanadia clusters, possibly monomeric VO_x species are found in the samples with vanadia loadings lower than that corresponding to a polyvanadate

monolayer. Both higher calcination temperatures and higher vanadium contents lead to polyvanadate monolayers. Higher calcination temperatures (873 K) also lead to chemical interaction between VO_x species and zirconia and to a formation of zirconium vanadate. Very low concentrations of bulk V_2O_5 phase are found in the catalysts with high VO_x surface density calcined at higher temperatures (873 K). Analysis of catalytic and spectroscopic data suggests that polyvanadates species highly dispersed on zirconia are active sites in propane oxidative dehydrogenation. The highest specific activity is observed for a surface density of $3\text{--}4\text{VO}_x/\text{nm}^2$ for VO_x/ZrO_2 calcined at 873 K. The propylene selectivity on this catalyst is 80%. At higher VO_x surface densities the specific activity declines monotonically, but the propylene selectivity remains constant [10].

The effect of the gas-phase oxygen partial pressure for the oxidative dehydrogenation of propane over a V-Mg-O catalyst was investigated to explore reasons for improved propylene yields when dehydrogenation was carried out under periodic operation. Steady-state experiments were performed in which the oxygen partial pressure was varied over a large range at constant propane partial pressures. In addition, the catalyst mass was varied to control the propane conversion so that selectivity and yield could be compared at a constant propane conversion. At the same propane conversion, propylene selectivity increased as the partial pressure of oxygen decreased. Thus, propylene yields can be improved at steady state by employing low oxygen partial pressures. It is likely that this is the reason for the higher propylene yields observed under unsteady-state or periodic operation. It appears that the reaction mechanism must consist of more than one pathway for production of carbon oxides

Improvement in propylene yields in oxidative dehydrogenation through periodic operation over a fairly wide range of cycle periods was explained by superior selectivity obtained in the absence of gas-phase oxygen in the portion of the cycle in which dehydrogenation proceeds. This contribution that it is possible under some operating conditions to obtain a similar propylene yield at steady state with the same time-average feed rate of propane by using a much lower concentration of oxygen in the feed. However, is restricted to low feed concentrations of propane. At higher concentrations, as the oxygen feed concentration is lowered, the improvement in

selectivity is accompanied by a decrease in propane conversion so that no improvement in yield is obtained. In this situation, periodic operation is superior to any steady-state operation at comparable conditions. Steady-state data were also obtained with different masses of catalyst at which oxygen concentrations were varied widely at a constant propane partial pressure. The variation in catalyst mass could be used to control the propane conversion to some degree. With a low feed concentration of oxygen and a high catalyst mass, the same propane conversion can be achieved as with a smaller amount of catalyst and a higher oxygen concentration in the feed. Propylene selectivity, however, is higher at the lower oxygen concentration. The complex relationship between oxygen concentration and selectivity cannot be explained simply by the inverse relation between selectivity and conversion expected for a consecutive reaction. There appears to be an additional pathway for the production of carbon oxides that depends on the partial pressure of oxygen [12].

The use of vanadate-exchanged magnesium-aluminium layered double hydroxides as precursors of mixed-oxide catalysts provides materials differing in catalytic performance depending on the nature of intercalated vanadate. The most active in the oxidative dehydrogenation of propylene is the sample derived from the decavanadate-exchanged LDH. The overall activity of the $\text{MgAlV}_{10}\text{O}_{28}\text{-MO}$ catalyst is, depending on temperature, comparable or slightly better than the reference 24VMgO sample prepared in a conventional way. The much higher intrinsic activity of this catalyst with respect to the 24VMgO sample is assigned both to the higher density of the surface vanadium sites and to their higher specific activity. The $\text{MgAlV}_2\text{O}_7\text{-MO}$ catalyst is the least active of all samples studied. Analysis of the selectivity-conversion profiles indicates that propylene formed in the oxidative dehydrogenation reaction is subsequently oxidized mainly to CO, the process being favoured over $\text{MgAlV}_{10}\text{O}_{28}\text{-MO}$ catalyst. The latter effect is related to the highest acidity and the lowest basicity of this catalyst, making the desorption of the propylene molecules more difficult. The performance of the $\text{MgAlV}_2\text{O}_7\text{-MO}$ sample changes upon conditioning in the reaction mixture to approach those of other samples, indicating that surface transformation is required for this sample to reach a steady state performance [14].

Vanadium and niobium oxides supported on TiO_2 are active in the oxidative dehydrogenation (ODH) of propane. Although niobia/titania catalyst is also able to catalyze the ODH of propane, its low activity indicates that in vanadia containing catalysts a vanadium oxide species must be involved in the paraffin activation as the activity increases with vanadium content, both in the absence and in the presence of niobium. The interaction between vanadium and niobium in the ternary catalysts modifies the surface acidity of the sample leading to the formation of active centers different from those present on vanadia binary catalysts. Redox properties are less affected by this interaction and are probably involved in the alkane activation and in the selective step of the reaction as well. Propane is more easily activated than ethane but lower propylene selectivity was obtained compared to ethylene. All catalysts, however, promote the same reaction path for both paraffins. The formation of carbon oxides in the ODH of ethane is more sensitive to the structure of the catalyst than in the ODH of propane due to the greater oxidability of propylene that can probably occur in the same extent on sites of different nature [15].

The results obtained by the investigations carried out by transmission electron microscopy and FTIR augmented by CO and NH_3 spectroscopy indicated that the dispersion, structure and relative location of surface sites of vanadia catalysts are strongly affected by the nature of the support. Oxide carriers with high specific surface area, as H-Na/Y zeolite, SiO_2 and Al_2O_3 allowed a high dispersion of the VO_x species, which cover only a limited part of the support. In the case of MgO , the occurrence of a partial dissolution/re-precipitation of the oxide matrix results in the incorporation of a fraction of V^{5+} ions in the bulk of the catalyst. By loading TiO_2 and ZrO_2 of low specific surface area with an amount of VO_x species close to the monolayer capacity, a layer of VO_x species which cover almost completely the support was obtained. In such condition, a close proximity of active centres can be suggested. For all catalyst, except that supported on MgO , V-OH Brønsted acid groups are formed as a consequence of the dispersion of VO_x species. The results obtained by FTIR spectroscopy of adsorbed ammonia on the VZ catalyst indicated that V-OH Brønsted centres are located in the neighborhood of species bearing V^{5+} ions involved in V=O and V-O-V bonds, which are usually considered as the catalytic active species. Propylene molecules primarily produced by

oxydehydrogenation of propane could be adsorbed on the Brønsted acid sites, and then undergo overoxidation by reaction with one of the redox sites in the neighbourhood. This cooperative effect (presence of Brønsted sites in proximity of agglomerated redox sites) might account for the low selectivity of the V_2O_5/ZrO_2 and V_2O_5/TiO_2 catalysts. This feature should be less effective for V_2O_5/SiO_2 and V_2O_5/Al_2O_3 systems, where the dispersion of active sites is much higher and, in fact, they exhibit a high selectivity towards propylene. Though $V_2O_5/H-Na/Y$ catalyst contain highly disperse VO_x species, the presence of a large amount of Brønsted acid protons in its porous structure, where the catalytic active sites are located, results in the low selectivity of this system. Finally, the poor selectivity of the V_2O_5/MgO catalyst, where Brønsted acid sites were not detected, can be ascribed to the formation of a magnesium vanadate phase active in the total oxidation of propane [16].

Vanadium type catalyst support on Al_2O_3 , TiO_2 , ZrO_2 , and MgO were use in oxidative dehydrogenation of propane. The promotion of V_2O_5/Al_2O_3 with alkali metals (Li, Na, and K) was also attempted. Evaluation of temperature programmed reductions patterns showed that the reductivity of V species by the support acid-base character. V_2O_5/TiO_2 catalyst exhibits the highest activity in oxidative dehydrogenation of propane. The support nature also affects the addition alkali metals decrease the catalytic activity in the Oder non-dope $> Li > Na > K$. propane selectivity significantly increase in the presence of doped catalysts [22].

Zeolite Na-Y containing boron has very low activity in the oxidative dehydrogenation of propane. Oxide boron species behave as an inert component not interacting with the zeolite support. The effect of cations upon selectivity to olefin in the stabilized zeolite Y is not significant. The only exception is indium, which decreases olefin selectivity to a large extent. The presence of both In and Ga oxide species is not beneficial for the reaction selectivity. There is on marked difference in the oxidative dehydrogenation of propane on the stabilized zeolite Y modified with reducible (Ga, In, Sb, Sn) and not reducible (Ca, Mg) [23].

Recent activities in the preparation and characterization of the V-Mg-O catalysts for the oxidative dehydrogenation of alkane have advanced the

understanding of this catalysis system. It is now understood that a desirable feature of this catalytic system is the strong interaction of MgO with V_2O_5 , resulting in the formation of Mg vanadate. In this compound, the isolate or small VO_x units formed are desirable for high dehydrogenation selectivity, because they can supply only a limited number of oxygen atoms for reaction with adsorbed hydrocarbon species. While the same order support could also come from isolate VO_x units, they could do so only at low V concentrations. The fact that the selectivity for dehydrogenation depends strongly on the hydrocarbon is very interesting but not well understood. It appears that a better understanding of this phenomenon would be very informative towards the design of highly selective catalysts, and improvement of the V-Mg-O system [24].

The present study has shown that the redox elements such as Co, Fe, Ga, Ni, Sb or Zn are partly substituted during synthesis to Mo^{VI} in a $Cs_{2.5}H_{1.5}PV_1Mo_{11}O_{40}$ material, the remaining part being in cationic exchange position. This leads to catalysts quite active in propane oxidative dehydrogenation to propene at relatively low temperature (300-400°C). It has also been shown that using Cs salts leads to catalysts stable under our catalytic conditions. Relative acidity (via Keggin anion metallic substitution) and redox properties by exchange cations replacing the protons either during synthesis or post-synthesis can be tuned. However, it was also shown that the direct synthesis process was more efficient than post-synthesis cations exchange. The main conclusion is that one can get a quite high selectivity in propene at relatively low temperature and keep the heteropolyacid salt stable under catalytic conditions by using the $Cs_{2.5}$ salts of the V_1 substituted material and exchanging protons by a redox metal.

Moreover, it is shown that Brønsted acidity remains quite strong leading to acetic acid rather than acrylic acid during propane selective oxidation. At variance this acidity permits propane to be activated at relatively low temperature, i.e. to get high selectivity in propene if redox cations replace majority of protons. The main conclusion is that the number of strong Brønsted acid sites and redox properties can be easily tuned for such a system, which results in promising properties for eventual substitution of propane dehydrogenation in the current industry process by oxidative dehydrogenation [25].

Oxidative dehydrogenation of propane have been studied on Mo/ γ -Al₂O₃ catalysts with 13 wt.% of MoO₃ and promoted with Li. The addition of Li affects the structure and properties of supported molybdenum oxides species. The presence of Li replacing Bronsted acid sites would eliminate nonselective route of oxidation on acidic centers decreasing total activity. The Raman spectra shows a weakening of the Mo=O bond on Li-loaded catalysts. The change in the strength of the terminal Mo=O bond does not correlate with the decrease in Mo species reducibility or with the marked decrease in propane conversion. This behavior suggests that the terminal Mo=O bond is not the active sites for oxidative dehydrogenation of propane, since this bond become more labile upon interaction with lithium. Similar catalytic performance was obtained independently of the sequence of Li addition [26].

The Ni_xMg_{1-x}Al₂O₄, NiCr₂O₄, and MgCr₂O₄ spinels have been synthesized, characterized with the XRD and XPS methods, and tested in the oxidative dehydrogenation of propane. The crystallochemical model of solid surfaces, CMSS, has been used to calculate the oxygen cation's bond energies in the spinels. For the NiMgAl spinels the activity and selectivity to propylene increase with the increase in the Ni content. The Ni ions surrounded by oxygen in the spinel structure are proposed as active centers for oxidative dehydrogenation to propylene. The NiCr spinel is more active but less selective than the NiMgAl spinels; the difference in catalytic behavior has been ascribed to different coordination of Ni ions in the two groups of the spinels and to the lower oxygen cation's bond energy in the NiCr spinel. In the Ni_xMg_{1-x}Al₂O₄ system the activity and selectivity in the ODH of propane increase with the increase in the Ni content. It is suggested that the Ni–O centers are active in oxidative dehydrogenation of propane to propylene. NiCr₂O₄ spinel shows higher activity and lower selectivity to propylene (at comparable propane conversions) as compared with the NiMgAl spinels. The comparison of the catalytic behavior of MgCr₂O₄ and NiCr₂O₄ with that of MgAl₂O₄ suggests that Cr–O centers in the spinel structure also participate (though to the smaller extent than Ni) in the propane–oxygen reactions.

It is suggested that the differences in the activity and selectivity observed for the NiMgAl and NiCr spinels may be due to different coordination of Ni ions (confirmed by the XPS measurements): octahedral in NiMgAl and tetrahedral in NiCr

systems. The higher activity and lower selectivity of the NiCr spinels may be also due to the lower oxygen cation's bond energy in these systems [13].

The presence of vanadium on MgO changes the surface area of V-Mg-O. The content of vanadium increase the surface area sharply. However, the surface area of V-Mg-O decreasing vanadium content. Alkali metal loading has effect on the surface area of 28V-Mg-O. The order of decreasing surface area of catalysts are as follow: Li > Na > K. the active species on 28V-Mg-O surface are VO₃ and V-O-V. alkali metal induced into 28V-Mg-O can form V-M-O and/or M-O-M structure on the catalyst surface apart from V-O-V species, where M is alkali. IR spectra confirm the absent of V=O bond on V-Mg-O surface. Alkali loading on 28V-Mg-O increase the propane selectivity with decreasing the propane conversion. The catalyst performance of V-Mg-O catalyst pretreated in non-oxidizing atmosphere is better than that of catalyst pretreated in oxidizing atmosphere [30].

2.2 spinel material

Nanocrystalline and nanoporous zinc aluminate spinel with high specific surface area and narrow pore size distribution has been successfully prepared by hydrothermal treatment of basic aluminium nitrate and zinc acetate, at a relatively low temperature. Powder X-ray diffraction and transmission electron microscopy confirmed that the as-prepared material was a pure ZnAl₂O₄ phase with a quasi-spherical morphology. The synthesis described there, in contrast to other methods, do not required high temperature calcinations to obtain the spinel phase. The properties of the hydrothermally obtained zinc aluminate spinel make it a promising material for use in the development of thermally stable catalysts and supports for high-temperature processes such as combustion of light hydrocarbon or complete oxidation of organic pollutants and CO from exhaust and industrial gas [27].

Controlled hydrolysis of mixed metal isopropoxides, followed by calcination at mild temperature, was shown to be convenient method for preparing high surface area Zn-Al oxides having a spinel type structure. The main advantage of this preparation procedure are high control on the purity of the resulting materials, and

mixing of the precursors at the molecular level, which facilitates formation of homogeneous product at a low calcination temperature. The material obtained had unimodal pore radii distributions with maxima in the 1.5-2 nm range, and surface areas in 126-288 m²/g range. Both of these properties are desirable features for potential applications in the field of heterogeneous catalysis. Lewis type surface acidity, mainly due to coordinatively unsaturated Al³⁺ ions, was found to be to the same order as that shown by gamma alumina, as determined by IR spectroscopy of adsorbed carbon monoxide [28].

Low-temperature synthesis of nanocrystalline zinc aluminate spinel (ZnAl₂O₄) from single alkoxide molecules, [ZnAl₂(OR)₈], is described. The ideal Zn:Al stoichiometry, with respect to the 2–4 spinel phase in the molecular precursor, results in the formation of monophasic ZnAl₂O₄ at 400°C, which is significantly lower than the temperatures reported for the synthesis of crystalline ZnAl₂O₄. The correlation of crystallite size and the optical properties of the prepared ZnAl₂O₄ nanoparticles shows an inverse relationship between the bandgap values and particle size. The optical properties show that ZnAl₂O₄ is a better candidate than ZnO for UV reflective coatings. The structural investigations using solid-state ²⁷Al NMR indicate that ZnAl₂O₄ is partially inverse at lower temperatures (900°C, degree of inversion 0.3); however, the regular spinel structure is obtained at 1000°C. A comparison of the average crystallite size obtained from the electron microscopy and powder diffraction data shows that the number-weighted (TEM) and volume-averaged (XRD) particle sizes are comparable, which corroborates the narrow size distribution found in the spinel particles in our experiments. A comparison of the valence-band spectra of ZnAl₂O₄ and ZnS suggests that O 2p–Zn 3d hybridization may be responsible for the lowering of the bandgap in ZnAl₂O₄ [29].

Physical properties and thermal stability of zinc gallate and zinc aluminate can be controlled by the reaction of crystallite formation besides reaction condition and strength of the alkyl group of the metal alkoxides. The reaction of crystallite formation occurring rapidly, the crystallization of products occurred rapidly too, therefore as-synthesized products were well-crystallized spinel, high surface area and high thermal stability.

The thermal stability of zinc gallate and zinc aluminate product did not depend on type of solvents used in synthesis. But depended on crystallite sizes of them. The type of the second metal influent on the thermal stability and rate of thermal stability decreasing of the metal oxide differently [20].



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย