

# Catalytic Dehydration of Methanol to Dimethyl Ether (DME) Using the $Al_{62,2}Cu_{25,5}Fe_{12,3}$ Quasicrystalline Alloy

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## Abstract

Dimethyl ether (DME) has been considered a potential and promising energy alternative for petroleum subproducts due to its good burning characteristics, and to its high cetana content which is superior to that of diesel. Furthermore, DME can be considered a cleaner fuel than diesel. DME can be produced by dehydration reaction of methanol by using solid catalysts in catalytic reactions. This study shows an analysis of the performance of  $Al_{62,2}Cu_{25,5}Fe_{12,3}$  quasicrystalline alloy as catalyst for dehydrating methanol to produce DME. These quasicrystalline alloys are stable at high temperatures, show a low thermal conductivity and exhibit a fragile nature, which turn them to be easily crushed. Also, their activity is not affected by water. In this research it were used the following special measurements: (i) X-Ray Diffratometry (XRD) for analyzing the phases evolution of the alloys; (ii) Scanning Electron Microscopy (SEM) in order to study the surface microstructure and (iii) Transmission Electron Microscopy-TEM for studying internal phases; quasicrystal nuclei morphologies, initial defects and for testing methanol catalytic conversion and selectivity. The latter characteristics were also analyzed for DME and for other subproducts formed in the catalyst. The study showed a good performance of the  $Al_{62,2}Cu_{25,5}Fe_{12,3}$  quasicrystalline alloy used as catalyst for DME production.

**Keywords:**  $Al_{62,2}Cu_{25,5}Fe_{12,3}$  quasicrystalline alloy; Dimethyl ether (DME); Methanol dehydration

## Introduction

Dimethyl ether (DME) has attracted a worldwide attention because of its potential as an alternative for substituting petroleum. Its use in diesel motors causes low emissions of soot particles and of  $NO_x$  [1]. Hence, it can be considered an environmentally compatible fuel. DME production has been investigated by several researchers in many parts of the planet.

At environmental conditions; i.e., at 1 atmosphere pressure and temperature of 25°C, DME is present in gaseous state. When it is submitted to higher pressures or to lower temperatures it liquefies easily in the same way as PLG (Petroleum Liquefied Gas) [2].

Probably in next future, DME can be stocked and distributed by using almost the same technology applied to PLG. Hence, DME can be applied as a PLG substitute although it presents a thermal power lesser than that of propane gas ( $C_3H_8$ ) and butane gas ( $C_4H_{10}$ ) which are the main constituents of this fuel [3]. Furthermore, it is important to state that there is an increase in the use of DME as thermoelectric energy.

DME is generally produced when methanol is dehydrated according to the following chemical reaction [4]:



$$(\Delta G = -12,1 kcal.mol^{-1}, 25^\circ C)$$

where  $\Delta G$  refers to the standard free energy for the reaction given by equation (1).

Several researches were performed in order to formulate better the use of catalyst solids such as crystalline solids, amorphous, zeolites, and quasicrystalline solids. The principal aims of these researches were to

ensure not only a higher stability during the catalytic reaction but also to optimize DME production [5].

Recently, quasicrystals are been applied in catalyst reactions due to its stable equilibrium phases even at high temperatures. The quasicrystalline materials occupy a position between crystal and amorphous materials. They exhibit a complex structure showing a repetition of quasiperiodicity in the atoms arrangement together with rotational symmetries which are not observed in crystals [5].

The catalytic behavior of the  $AlPdMn$  quasicrystalline alloy was investigated in comparison with that one of pure  $AlPd$  crystals, pure copper and pure iron crystals. In the research, particles with size less than 200nm of each sample were mixed with magnesium oxide ( $MgO$ ) and were calcined at 775K during 5 hours [6]. In the reaction of methanol decomposition, the quasicrystal catalyst achieved a great amount of hydrogen gas at low temperature in the beginning of the reaction. Several palladium quasicrystals alloys were tested and they showed to be highly active for methanol decomposition.

The first vapor reform reaction by using  $Al_{62,2}Cu_{25,5}Fe_{12,3}$  quasicrystal was obtained after lixiviation of the alloy giving an  $H_2$  production

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of 235 L.  $kg^{-1}.min^{-1}$  at 553°C [7]. In catalytic reactions there was also formation of other metalorganic products such as dimethyl ether (DME); methanoic acid and others [8].

This study shows the behavior of  $Al_{62,2}Cu_{25,3}Fe_{12,5}$  quasicrystal alloy in catalytic reactions and its applicability for obtain DME from the methanol dehydration.

## Theoretical Considerations

### Methanol dehydration Synthesis to DME

DME is obtained from the synthesis gas which is a mixture of carbon monoxide and hydrogen gas originated from natural gas reform, from petroleum subproducts, from gaseous coal and from biomass (Bio-DME). In this process, the synthesis is achieved from two distinct catalytic functions: hydrogenate and dehydration functions, respectively [9]. The first one is based in the initial methanol formation and produces the synthesis gas. The second one is related to DME production from condensation of two molecules of methanol. In both processes, reactions take place through a catalyst which can be metallic solids, amorphous solids, crystals, semiconductors, zeolites and quasicrystalline alloys.

The main reactions observed in DME synthesis are a reaction limited by the equilibrium of methanol syntheses and a reaction not limited by the equilibrium of the methanol dehydration in catalysts [10].

Reactions involved in this process are as follows [11]:

- Reaction for methanol synthesis defined as:



with enthalpy value given by  $\Delta H = -43,2 \text{ kcal}.mol^{-1}$ .

- Reaction for methanol dehydration given by:



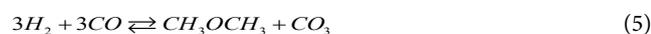
in which enthalpy value is  $H = -5,6 \text{ kcal}.mol^{-1}$ .

- Water – gas reaction:



With enthalpy value given by  $\Delta H = -9,8 \text{ kcal}.mol^{-1}$ .

The overall reaction is given by:



In which enthalpy value is  $\Delta H = -58,6 \text{ kcal}.mol^{-1}$  and the product of each reaction is the reactant of the reaction given by equation (5).

The hydrogen formed in the reaction of equation (4) is the reactant for synthesizing methanol. This allows a high conversion of the synthesis gas in the overall reaction according to equation (5). It is important to state that the combination if these reactions results in a synergic effect making easier not only the thermodynamics of methanol synthesis but also the reactions of displacement associated to water-gas. Normally, the latter reactions are observed in solid catalysts such as quasicrystals, zeolites, crystal solids, amorphous solids, metallic solids and semiconductors because the catalysts can support high temperatures around 500°C [12].

Regarding the use of zeolites as catalysts, the studies have showed that when methanol is catalyzed on the surface of acid zeolites firstly it

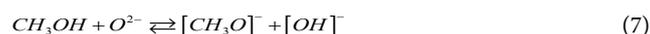
dehydrates producing DME and secondly the mixture is converted in olefins and aromatic aliphatic compounds until  $C_{10}$  [13].

The mechanism of methanol adsorption, its dehydration, the C – C first liaison formation as well as the nature of intermediaries compounds involved in the reactions are not entirely understood [14]. Kasaie and Sohrabi suggested that methanol reaction occurs in Brønsted site and its adjacent locals in the Lewis basic sites forming both  $[CH_3 - OH_2]^+ + [CH_3O]^-$  species in the quasicrystal surface. Afterwards, when it condensates DME and water are produced [15]. This kinetic mechanism utilizes Langmuir-Hinshelwood to explain the heterogeneity of the catalytic reaction on the quasicrystal surface and is based in the studies of Bandiera et al. [16].

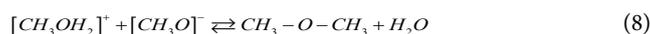
Methanol molecules are adsorbed in two different types of sites: acidic site (Lewis) and basic site (Brønsted) [17]. Initially, in the catalyst surface occurs the adsorption of one proton of  $H^+$  according to the following equation [18]:



Simultaneously, methanol molecules are adsorbed in the basic site giving:



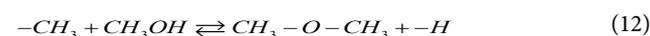
The above species are then adsorbed on surface producing DME by condensation according to the following equation:



The catalyst surface is regenerated by the following reactions:



According to Kubelková et al. [19], only one molecule of methanol is adsorbed on the surface with one transition of protonated  $H^+$ . After dehydration, one methoxy group remains in the surface. Another molecule of methanol reacts with DME methoxy group according to the reaction given by:



### Methanol dehydration to DME in quasicrystal catalytic reaction

When transition metals are used as catalysts, especially in steam reform reaction, being or not supported, they must show a very well defined structure. In the active phase dispersion, the metallic ions oxidation states define the “d” (electronic sublevel) character and the atomic radius [20]. These factors have a great influence in the selectivity and activity of catalysts. The metallic ions used as dopants show a lesser size and valence than these of the supported ion used. When the ions of low valence are substituted by ions of high valence, spaces in the structure of the crystalline solids are formed. In this case, it is observed the presence of gaps for the oxygen atoms which are interlinked in the  $SiO_2$  net [21]. These vacancies exhibit an important role in the stabilization of catalytic systems.

The catalytic dehydration of methanol on the quasicrystalline alloy  $Al_{62,2}Cu_{25,3}Fe_{12,3}$  catalyst is due to oxidation reaction of methanol + methanoic acid, DME and intermediary products. One of the advantages of this type of catalyst is that in the beginning of the water reaction in gaseous state there is no blockage in the local active sites.

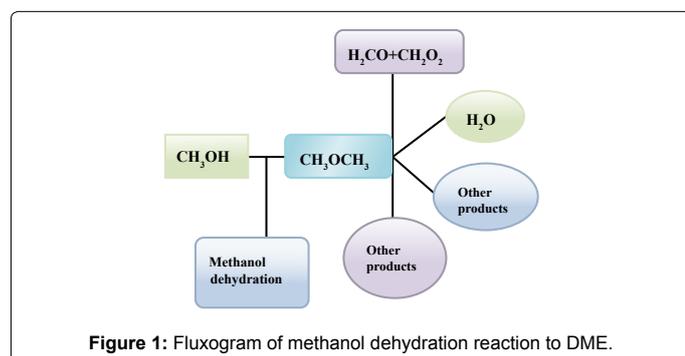


Figure 1: Fluxogram of methanol dehydration reaction to DME.

Therefore, the reaction products show a better selectivity due to a lesser formation of weak acid sites. Figure 1 below illustrates the dehydration reaction of methanol in the  $\text{Al}_{62,2}\text{Cu}_{25,3}\text{Fe}_{12,3}$  quasicrystalline alloy.

Experimental results show that the methoxy radical ( $-\text{O}-\text{CH}_3$ ) is the intermediary more stable product formed after methanol adsorption in the quasicrystal surface. With increase in temperature this species is decomposed into formaldehyde ( $\text{H}_2\text{CO}$ ). It is important to state that in the iron (Fe) surface occurs methane formation ( $\text{CH}_4$ ). As to copper (Cu) surface, the methoxy radical is adsorbed much easier in gaps of energy. This process is observed in the top of surface in the (111) crystallographic plane formation or near the first saturation layer of the adsorbed atoms. It was observed later that the methoxy radical is adsorbed in all adsorption sites of the copper surface in  $\text{Al}_{62,2}\text{Cu}_{25,3}\text{Fe}_{12,3}$  quasicrystalline alloy. This is due to the layer that exhibits valence 3d, 4s and 4p sublevels which effectively influence the catalytic sites of the catalyst [22]. In this process, part of the methanol formed comes from the copper interaction with reaction substrate in the quasicrystal surface. Copper has a tendency to oxidize by using the oxygen present in the catalyst surface and thus producing copper oxide ( $\text{CuO}$ ) and copper hydroxide ( $\text{Cu}(\text{OH})_2$ ) species [23]. There is also a possibility for ion pairing between copper and magnetite ( $\text{Fe}_3\text{O}_4$ ) forming copper ferrite ( $\text{CuFe}_2\text{O}_4$ ) and between copper and iron oxide forming delafossite ( $\text{CuFeO}_2$ ). All these substances show good electrical properties for metallic conduction [24]. In the quasicrystal surface an initial oxide layer is observed when temperature reaches  $670^\circ\text{C}$  [25]. This is a passivation layer that is comprised of a thin oxide film. The mass of aluminum atoms formed in the quasicrystal surface is due to a directional force supplied by oxide exothermicity which is greater than all the others species of the alloy. It was also observed that  $\text{Al}(\text{CuFe})+\text{AlFe}_3$  quasicrystalline alloy when submitted to temperature of  $350^\circ\text{C}$  produces, during the reaction process, the  $\text{Al}_7\text{Cu}_2\text{Fe}_2$  chemical that exhibits a tetragonal form [26]. Hence, it is observed oxidation in both aluminum and copper. In the range of temperature  $425^\circ\text{C}$  to  $550^\circ\text{C}$  this chemical prevails, but associated to ferric aluminum traces ( $\text{Al}_2\text{Fe}_3$ ). This fact shows that an increase of  $125^\circ\text{C}$  in temperature is sufficient for oxidizing the quasicrystalline alloy. Aluminum of the qc surface also acts as an acid function for catalyzing the DME hydrolysis to MeOH ( $\text{CH}_3\text{OH}$ ). On the quasicrystal surface, aluminum forms aluminum hydroxide ( $\text{AlOH}$ ). These agglomerates together with the reaction elements (hydrogen, oxygen and carbon) make arrangements with linking of clusters and represent the quasicrystal acid site. The reaction of one molecule methanol is initially absorbed in the qc local site. Then, methanol is dehydrated leaving a methyl group linked to the oxygen of the qc structure of this arrangement.

## Experimental Methodology

### Preparation of the $\text{Al}_{62,2}\text{Cu}_{25,3}\text{Fe}_{12,3}$ quasicrystalline alloy

In the preparation of the precursory alloy to be applied as

catalyst, it was utilized  $\text{Al}_{62,2}\text{Cu}_{25,3}\text{Fe}_{12,3}$  ternary system. Powders with nominal composition of  $\text{Al}_{62,2}\text{Cu}_{25,3}\text{Fe}_{12,3}$  were classified in terms of its granulometry and prepared with purity superior to 99,90%. The alloy was obtained by applying air fusion to the pure elements. Induction oven controlled by Argonium 5, 0 atmospheres was utilized. The alloy was then submitted to several foundries in order to ensure the complete dissociation of its components and to achieve a good homogeneous quasicrystalline phase. The samples were prepared at the Fast Solidification Laboratory, - LSR of the Federal University of Paraiba, UFPB by utilizing a high frequency POLITRON generator (40kVA). For the preparation of the alloy it was weighed 10g of the samples by using a SHIMADZU AY220 model balance (precision around  $10^{-4}\text{g}$ ). The alloys were formed by applying the solidification method in a special oven and, thus, results a mixture of quasicrystalline and crystalline league. For this purpose, it was used a NABERTHERM resistance oven where the samples were submitted to a temperature of  $750^\circ\text{C}$  during 8 hs and 24 hs, respectively. After this procedure, samples were placed in induction oven at argonium rare-effect atmosphere. Samples were heated in a rate of  $30^\circ\text{C}\cdot\text{min}^{-1}$ . For catalytic reactions and to avoid decrease in the oxidation reaction, samples were encapsulated in a quartz tube under continuous vacuity during thermal treatment.

X-Ray Diffractometry (XRD) tests were applied in order to follow the phase evolution and the samples stability during the melting process. It was used a SIEMENS DIFFRATOGRAM D 5000 and it was applied  $\text{CuK}\alpha$  radiation with wave length of  $\lambda = 1,5406 \text{ \AA}$ . The tests were performed at a temperature of 298K, 40Kv tension, 30mA electric current, step of  $0,01^\circ$ , time by step of 3s and angle of  $2\theta$  (2-theta) with variation of  $20^\circ$  to  $120^\circ$ .

Scanning Electron Microscopy (SEM) tests were applied for analyzing quasicrystalline surface morphology by using a LEO MODEL 1430 scanning electronic microscope coupled to an OXFORD probe. Samples after been melted and submitted to catalytic tests were immersed in isopropyl alcohol solution. Afterwards they were placed in a DABIATLANTE-3L Ultrasonic Cable in order to promote the powder non agglomeration. After this procedure, samples were analyzed for SEM.

Dispersive Energy Spectroscopy (DES) in samples was obtained in the micrographic of dispersive energy analysis after thermal treatment of 24 hs coupled to SEM analysis. The samples were previously metalized with gold in a medium thickness of 12 nm.

The experimental analysis performed in the Transmission Electronic Microscope (TEM) used a TECNAC 20 Model with tension between 20 to 200 kV,  $1,9 \text{ \AA}$  and point resolution of 0,2 nm. The tests helped to describe not only the quasicrystal structure but also the samples morphology and thus propitiating informations such as surface defects, discordances and particles size.

### Catalytic tests on the $\text{Al}_{62,2}\text{Cu}_{25,3}\text{Fe}_{12,3}$ quasicrystalline alloy

The catalytic tests were performed in the catalytic evaluator reactor, TCAT-1 Model, at atmospheric pressure. In general, methanol concentration in the admission gas has always increased to 18.6% (in molar unity). The rest was a mixture of air,  $\text{N}_2$  and methanol, generally of argonium (37%) +  $\text{N}_2$  (18.4%) + methanol (26%). For the tests it was weighted 300 mg which was introduced into a U reactor of Pyrex glass. This vessel was heated at environmental temperature until  $450^\circ\text{C}$  in argonium in a heat rate of  $20^\circ\text{C}\cdot\text{min}^{-1}$ ,  $50 \text{ mL}\cdot\text{min}^{-1}$  flux [27].

After reaching the temperature of  $450^\circ\text{C}$ , the sample stayed at this

condition during 2 hours in order to remove the physically fissored water.

The following procedure was to transfer the methanol from a saturator at environmental temperature to the catalytic bed through a heated line at 120°C with air flow of 50 mL.min<sup>-1</sup>. During the reactive process, the catalytic bed was maintained at a constant temperature of 450°C by using a COELHW1500 temperature controller. The effluent products of the reactor were successfully “online” injected by means of a 10 ways valve in a VARIANCP 3800 gas chromatograph. This experiment has a thermal conductivity detector in intervals of 15 minutes until it reaches the pseudo – stationary state. Experimental tests were made with six consecutive injections at intervals of 15 minutes and, thus, totalizing 90 minutes.

## Results and Discussions

### X-Ray Diffratometry results

X-Ray Diffratometry spectra of  $Al_{62,2}Cu_{25,3}Fe_{12,5}$  quasicrystal samples are shown in Figure 2 and 3, respectively, for thermal treatments of 8 hs and 24 hs. This phase shows clearly that the sizes of the grains are critical to initiate the already existing transformation. In these peaks can be noticed the quasicrystalline icosahedral phase (i) and the crystalline phase ( $\beta$ ) with  $Al_{50-x}(Cu, Fe)_{50+x}$  composition [28].

In these figures it can be recognized the quasicrystalline icosahedral i-phase,  $\beta$ - $Al_{0,5}Fe_{0,5}$  phase, tetragonal phases such as  $\theta$ - $AlCu_2$ ,  $\theta$ - $CuAl_2$  which can be identified in the peaks. Generally,  $\beta$ -phase coexists with the quasicrystalline phase when the applied process does not propitiate the thermodynamic conditions for the alloy to be completely quasicrystalline. Hence, it is formed the icosahedral phase. By comparing Figures 2 and 3 it can be noticed that the peaks for  $\beta$ -phase suffer a displacement to the left. When thermal treatment is accomplished (in 24 hs), the quasicrystalline alloy is homogeneous and the alloy is practically monophasic; i.e., this is the required time to ensure the sample saturation. This technique allows characterizing the purity of the phase which is termed “bulk”. The spectra are in accordance to ROSAS and PEREZ [29], once they define this phase as a solid solution for controlling the formation of quasicrystalline phase.

### Scanning electronic microscopy (SEM) and energy dispersive spectroscopy (EDS)

Figures 4a, 4b, 5 and 6, respectively show the results obtained by using Scanning Electronic Microscopy and EDS in the samples before and after the catalytic reactions. Figures 4a and 4b show, respectively,

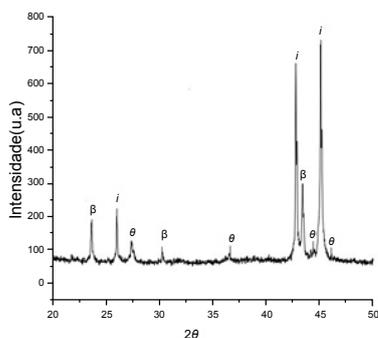


Figure 2: X-Ray Diffratometry for  $Al_{62,2}Cu_{25,3}Fe_{12,5}$  sample with thermal treatment in 8 hs.

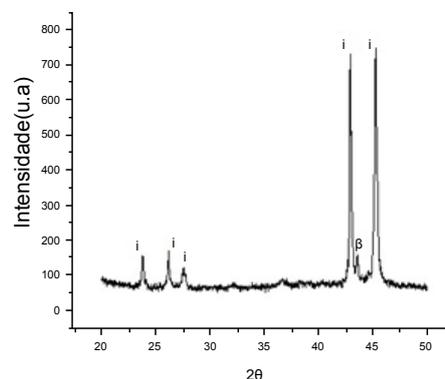


Figure 3: X-Ray Diffratometry for  $Al_{62,2}Cu_{25,3}Fe_{12,5}$  sample with thermal treatment in 24hs.

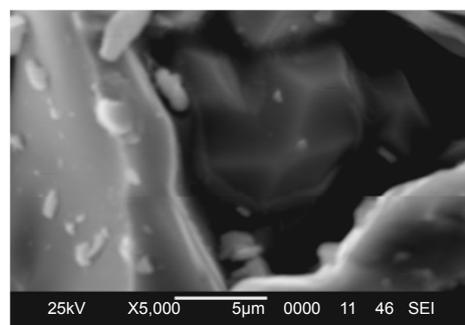


Figure 4a: Image obtained of the  $Al_{62,2}Cu_{25,3}Fe_{12,5}$  quasicrystalline alloy showing the icosahedral phase in 24 hs.

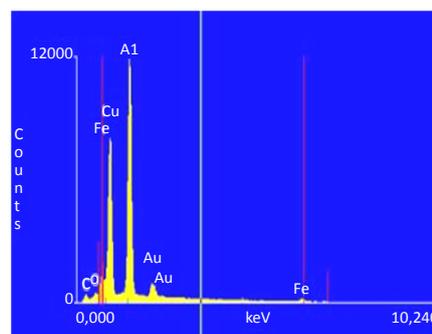
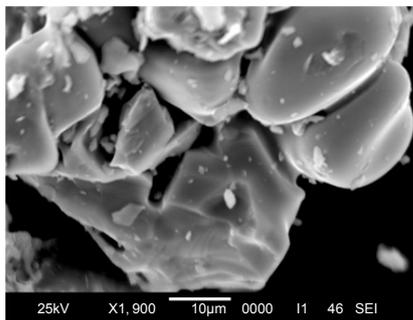


Figure 4b: SDE elementary analysis of  $Al_{62,2}Cu_{25,3}Fe_{12,5}$  quasicrystalline alloy showing icosahedral phase after thermal treatment in 24 hs.

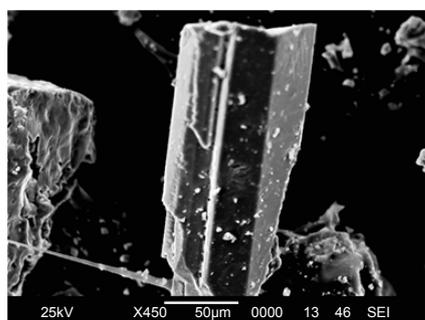
the results of SEM and EDS applications in samples after thermal treatment of 24 hs.

In Figure 4a it is observed a very good geometrical uniformity which is a result of cleavage fractures, a bit rough, with icosahedral symmetry, but with some porosity. On the surface it is possible to notice quasicrystalline grains in the form of dodecahedral polyhedrons. In Figure 4b, it is observed a major predominance of aluminum in relation to others quasicrystalline alloy components.

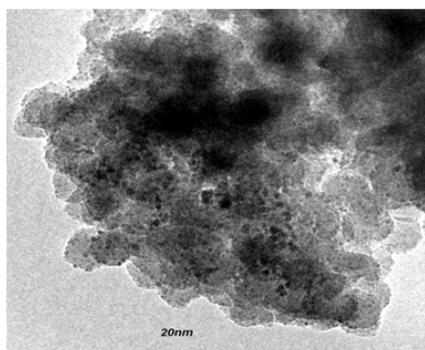
Figures 5 and 6, respectively, show the results of the SEM measurements applied in the samples after catalytic reaction.



**Figure 5:**  $\text{Al}_{62.2}\text{Cu}_{25.3}\text{Fe}_{12.5}$  quasicrystalline alloy with 8hs of thermal treatment and submitted to catalytic reaction.



**Figure 6:**  $\text{Al}_{62.2}\text{Cu}_{25.3}\text{Fe}_{12.5}$  quasicrystalline alloy with 24 hs of thermal treatment and submitted to catalytic reaction.



**Figure 7:** Image of TEM-Transmission Electronic Microscopy for  $\text{Al}_{62.2}\text{Cu}_{25.3}\text{Fe}_{12.3}$  quasicrystalline alloy sample after thermal treatment of 24 hs.

The microstructure of the sample which is illustrated in Figure 5 shows nodules formation in the catalyst surface due to an oxide  $\theta$ - $\text{Al}_2\text{O}_3$  layer formation which is non homogeneous. This layer penetrated the  $\text{Al}_{62.2}\text{Cu}_{25.3}\text{Fe}_{12.5}$  alloy surface and allowed  $\alpha$ - $\text{Al}_2\text{O}_3$  formation. Hence, it is evidenced a superficial nodule morphology that has almost 5% of copper. In this figure, it is observed a decomposition of quasicrystalline phase to crystalline phase due to the increase in temperature of catalytic reaction. This reaction has occurred in temperature above  $400^\circ\text{C}$  and formed initially on the whole qc surface, an amorphous oxide layer. This process is due to nucleation and oxide crystallites growth in the  $\gamma$ - $\text{Al}_2\text{O}_3$  phase which is distributed in aleatoric form in the interface between metal oxide and the amorphous. This growth is fed by diffusion to the metal/oxide interface. The atomic oxygen of the amorphous layer is generated through fissures of the amorphous layer.

Naturally, it has occurred the reduction in quasicrystalline phase and an oxidation in intermetallic phase which, in its turn, acted as nuclei or catalytic sites.

### Transmission electronic microscopy-TEM

Due to the existence of icosahedral quasicrystalline phase (crystalline and intermetallic phases) it was applied TEM-Transmission Electronic Microscopy for analyzing the structure characterization of the samples. Figure 7 shows the quasicrystalline alloy after thermal treatment of 24 hs and at temperature of  $750^\circ\text{C}$ .

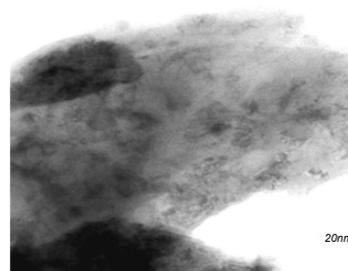
In Figure 8 it can be observed the quasicrystalline alloy microstructure after thermal treatment and after catalytic reaction.

In both figures, it is possible to visualize particles agglomerates morphology in a range from  $8 \cdot 10^{-1}$  nm to 20nm after catalytic reaction. Also, in those figures, it can be seen an image of dark areas in which occurred various morphologies of the phases.

Nature of metallic particles was confirmed by EDS-Energy Dispersive Spectroscopy and showed preferential localization according to the metal. Regarding Cu, its metallic particles are located in the quasicrystal edges. In these regions, it is possible to find big copper crystals indicating enrichment in the layer of the quasicrystal catalyst. In other words, there was a copper particle synthesizing during the catalytic reaction.

Faungnawakij et al. [30] stated that the iron addition to Cu/ZnO/ $\text{Al}_2\text{O}_3$  contributed significantly to conduct highly dispersed Cu particles formation. Fang et al. [31] Said that the addition of  $\text{FeO}_x$  to Cu/ $\text{Al}_2\text{O}_3$  gives rise to highly dispersed copper formation. As to iron, Fe it is important to notice its beneficial effect regarding the catalytic behavior through the interaction between copper and iron oxide ( $\text{FeO}$ ) and its oxides in catalysts of type (CuFe)-Cu/ $\text{FeO}_x$  or supported catalysts. This benefit refers to the increase in catalytic activity and to its good thermal stability. Other researchers showed a good relation of Cu single orientation to  $\text{Fe}_3\text{O}_4$  in which Cu took the same direction of  $\text{Fe}_3\text{O}_4$  reducing to a ferrite such as  $\text{CuFe}_2\text{O}_4$  (delafossite). In this case, its magnetic and electric properties are function not only of its ionic radius and valence but also from its chemical, morphological and stoichiometric properties and size of particles that propitiate the catalytic properties in chemical reactions [32].

Bergstein [33] related that the corresponding net in the interface between Cu and  $\text{Fe}_3\text{O}_4$  which is the reduced form  $\text{CuFe}_2\text{O}_4$  (delafossite) facilitates the formation of new metallic phases. Chen et al. [34] showed that the direct interaction between copper species and iron oxide



**Figure 8:** Image of TEM-Transmission Electronic Microscopy for  $\text{Al}_{62.2}\text{Cu}_{25.3}\text{Fe}_{12.5}$  quasicrystalline alloy sample after a catalytic reaction.

agglomerates could form new species to inhibit syntherization and increases the catalytic activity. In resume, dehydration reaction for methanol in copper surface originates the formation of DME and other intermediary products [35].

### Catalytic processes evaluation

Tables 1 and 2 show that  $Al_{62.2}Cu_{25.3}Fe_{12.5}$  quasicrystalline alloy has a very good performance. The synthesis of methanol to DME reached a good and satisfactory level of selectivity. Also, it occurs a good methanol conversion rate. From the results of these tables it was made the graph of Figure 9 with selectivity curves (%) related to time (minutes). These curves allow observing some behavior of the reactions products. Water curve remained constant and showed that there was no increase during vapor reaction. Generally, in this type of reaction and in the presence of  $Al_2O_3$ , it is observed a preferential tendency for water to be adsorbed in quasicrystal surface instead of methanol. This implies in a reduction in the methanol activity. However, in this case, there was no decrease in the methanol context ( $CH_3OH$ ). On the contrary, there was an increase in its conversion [36].

Acidity on the catalyst surface influences the products distribution as well as the catalytic activity. Hence, in the dehydration synthesis of methanol to DME, the selectivity is an important factor in methanol conversion. Figures 9 and 10 show, respectively, as a function of selectivity and conversion rate that DME efficiency rate has a good selectivity in this reaction. Two main factors must be considered: (i) the

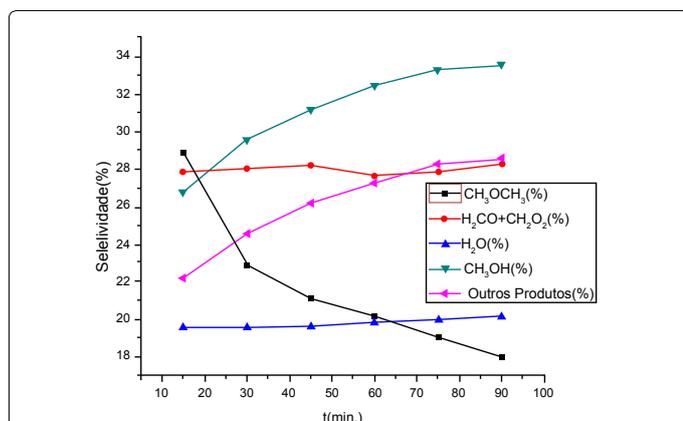


Figure 9: Catalytic behavior of  $Al_{62.2}Cu_{25.3}Fe_{12.3}$  quasicrystalline sample as a function of products selectivity (%) and time (min).

t(min.)	15	30	45	60	75	90
$CH_3OCH_3$ (%)	25,87	22,88	21,1	20,13	19,01	18,02
$H_2CO+CH_2O_2$ (%)	27,86	28	28,15	27,61	27,82	28,29
$H_2O$ (%)	19,54	19,56	19,6	19,85	19,93	20,12
$CH_3OH$ (%)	26,72	29,56	31,15	32,41	33,25	33,55
Other products. (%)	22,18	24,53	26,16	27,22	28,26	28,53

Table 1: Products selectivity (%) in methanol reaction as a function of injection time (min).

t(min.)	15	30	45	60	75	90
$CH_3OCH_3$ (%)	25,87	22,88	21,1	20,13	19,01	18,02
$CH_3OH$ (%)	26,72	29,56	31,15	32,41	33,25	33,55

Table 2: Conversion (%) of the catalytic reaction subproducts as a function of time (min.).

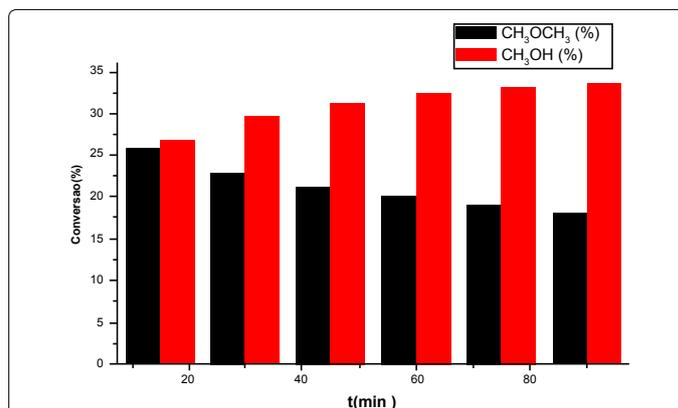


Figure 10: Comparison of conversion (%) of the catalytic reaction subproducts as a function of time (min).

presence of weak acid sites and that the water curve in all reaction time was constant and contributes in a satisfactory way to DME selectivity and (ii) the decrease of selectivity rate with time was not significant because of coke formation on the surface and that it was observed olefins production.

Methanal + methanoic acid subproducts ( $H_2CO+CH_2O_2$ ) showed its selectivity curve practically constant in the time intervals of the study. The analysis of methanol selectivity curve showed an increase of almost 10% during the time intervals of the research. This growth may be attributed to a total oxidation of methanol which was verified later in the reaction for methoxy radical production ( $CH_3O$ ) [37]. This radical is considered the more stable intermediary product after adsorption of methanol in qc surface. In the reaction as a function of methanol there is a decomposition of formaldehyde ( $H_2CO$ ). Normally, the next step after formaldehyde formation is the production in variable stages of carbon monoxide, CO or of carbon dioxide,  $CO_2$ .

In general, reactions occur in sequential stages. In the first stage, there is methanol dehydration. Next step shows that the hydrogen ion which is liberated can exothermally react with air giving rise to a reaction that is definitively an oxidative dehydrogenation. It is important to state that formaldehyde was produced as subproduct in the methanol dehydration. However, the aluminum which is present in the qc alloy gives some sites for formaldehyde production [38].

In terms of DME efficiency which is evaluated through the multiplication of methanol conversion, the results indicate that  $Al_{62.2}Cu_{25.3}Fe_{12.3}$  quasicrystalline alloy as catalyst shows a good stability in catalytic reaction and can be applied for methanol dehydration to DME.

### Conclusions

The main conclusions of this study are as follows:

1.  $Al_{62.2}Cu_{25.3}Fe_{12.3}$  quasicrystalline alloy used in the experiments is thermodynamically stable at high temperatures satisfying the initial requisite for utilizing it as a catalyst;
2. Iron and copper from the  $Al_{62.2}Cu_{25.3}Fe_{12.3}$  quasicrystalline alloy showed a direct interaction between copper species and ironed oxide agglomerates and thus making possible to produce new species in order to inhibit syntherization and to increase catalytic activity;
3. Copper particles (outside transition metals with  $3d^{n-2}4s^2$  energy sublevels) are observed in the quasicrystal surface. They

constitute the transition metallic element more favorable to the methanol oxidation reaction as well as methyl radical ( $CH_3$ ) formation. The latter constitutes the most stable intermediary product formed;

4. The quasicrystal  $Al_{62.2}Cu_{25.3}Fe_{12.3}$  catalyst proved to be adequate for dehydrating methanol to DME due to the good reaction performance. Its activity was not affected by water once it remained constant in the reaction process. The water in the reaction has a positive effect on the methanol dehydration because it regenerates the catalyst by removing carbon deposition and, thus, limits the deactivation due to coke production;
5. Aluminum present in the surface of  $Al_{62.2}Cu_{25.3}Fe_{12.3}$  quasicrystalline alloy propitiated aluminum oxide ( $Al_2O_3$ ) production, These agglomerates, together with reaction elements such as hydrogen, oxygen and carbon, formed link arrangements of cluster type representing the acid sites (Lewis and Brønsted sites) in the quasicrystal;
6. The metallic cations of the  $Al_{62.2}Cu_{25.3}Fe_{12.3}$  quasicrystal have the ability to form complexes (ion pairing) when react with water and can be represented by a general formulation such as  $[M(H_2O)_n]^{m+}$ ;
7. The low cost for producing this type of alloy for catalytic reactions constitutes one advantage and makes possible its use for industrial catalysts.

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