



## MAGNESIUM ALUMINATE CATALYZED PYROLYSIS OF n-HEPTANE

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### ABSTRACT

The effect of magnesium oxide precursor on the activity of magnesium aluminate catalyst for the pyrolysis of n-heptane has been investigated. Magnesium oxide was prepared either from magnesium acetate, magnesium nitrate, magnesium carbonate or hydrated magnesium oxide. In each case, magnesium aluminate (containing 28 wt.% MgO) was prepared. The prepared catalysts were characterized by X-ray diffraction, surface area and pore volume measurement, thermogravimetric analysis and chemisorption of carbon dioxide. Compared to noncatalytic pyrolysis, the conversion of n-heptane increased in the presence of each of the catalysts. Depending on the salt used for the preparation of MgO, the conversion, product yields and coke deposition were different. The cracking activity increased with an increase in the total basicity of the catalyst. Magnesium aluminate prepared using magnesium oxide obtained from magnesium acetate showed the highest conversion as well as the highest yields of ethylene.

**Key words:** Catalytic pyrolysis, Magnesium aluminate, N-heptane, Catalyst preparation.

### INTRODUCTION

Light olefins such as ethylene, propylene and butenes are usually produced by the noncatalytic steam pyrolysis of naphtha or light alkanes. Several research efforts have focussed on developing catalysts for pyrolysis and the limited data available on catalytic pyrolysis has been summarized elsewhere<sup>1,2</sup>. Most of the studies have used either calcium aluminates<sup>3-5</sup> or KVO<sub>3</sub>-based catalysts<sup>6,7</sup>. There is some published information to indicate that magnesium oxide or magnesium aluminate can also catalyze the pyrolysis reaction. Lemonidou and Vasalos<sup>5</sup> evaluated magnesium aluminate as a catalyst for the pyrolysis of n-heptane. They reported data for only one run, which shows that compared to noncatalytic pyrolysis, the yields of ethylene and propylene are significantly higher during catalytic

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pyrolysis. Taralas et al.<sup>8</sup> investigated the thermal and catalytic cracking of n-heptane in the presence of CaO, MgO or calcined dolomites. MgO was found to have the most pronounced effect on the conversion of n-heptane.

For MgO-based catalysts, the precursors can significantly affect the properties as well as the activity of the catalyst. Although no information is available on the effect of precursors on the properties of magnesium aluminate, some information has been published for MgO. Matsuda et al.<sup>9</sup> studied the properties of MgO prepared from various salts and the catalytic activity of these catalysts in 1-butene isomerization. Depending upon the source from which MgO was obtained, the basicity, one electron donor property and surface area were significantly different. They observed that the source of MgO had a significant effect on the conversion as well as the cis/trans ratio in 1-butene isomerization. Similarly, Choudhary et al.<sup>10</sup> reported that the surface properties (viz. acidity/acid strength distribution, basicity/base strength distribution, surface area, morphology and surface composition) of MgO obtained by thermal decomposition of magnesium hydroxide, magnesium nitrate, magnesium acetate or magnesium carbonate were widely different. They studied these catalysts for the oxidative coupling of methane and the catalytic activity and selectivity (for ethane and ethylene) of MgO obtained from magnesium carbonate and magnesium acetate were compared and these were much higher than that observed for MgO obtained from the other precursors.

The objective of the present investigation was to observe the physico-chemical properties of magnesium aluminate catalysts prepared from different magnesium salts and to study the effectiveness of these catalysts for the pyrolysis of n-heptane. For this, magnesium oxide was obtained from four different magnesium salts viz. magnesium acetate, hydrated magnesium oxide, magnesium nitrate and magnesium carbonate and subsequently magnesium aluminate catalyst was prepared using MgO and Al<sub>2</sub>O<sub>3</sub> in 1 : 1 molar ratio for use in n-heptane pyrolysis.

## **EXPERIMENTAL**

### **Catalyst preparation**

The magnesium aluminate catalysts were prepared by mixing the required amounts of MgO and Al<sub>2</sub>O<sub>3</sub> in the presence of a binder. MgO was obtained from either magnesium acetate, magnesium nitrate, magnesium carbonate or hydrated magnesium oxide. To prepare MgO from the acetate, Mg(CH<sub>3</sub>COO)<sub>2</sub> was mixed with deionised water to form a paste, which was then dried at 393 K for 12 h. The dried mass was calcined at 873 K for 2 h followed by calcination at 1173 K for another 2 h. A similar procedure was followed for the

preparation of MgO from  $\text{Mg}(\text{NO}_3)_2$ . To obtain MgO from the carbonate, magnesium carbonate was first prepared by precipitating it from an aqueous solution of magnesium nitrate by adding ammonium carbonate solution at a pH of 10-11 and 303 K. The precipitate was thoroughly washed with deionized water and then dried at 393 K for 12 h. The carbonate was decomposed at 873 K and then calcined at 1173 K for 2 h to obtain MgO. Magnesium oxide was prepared from hydrated MgO by slurring powdered MgO with deionized water for 4 h, and then drying the slurry at 393 K for 12 h.

To prepare magnesium aluminate catalysts, MgO and  $\text{Al}_2\text{O}_3$  in a molar ratio of 1 : 1 were mixed in the presence of a binder to form a paste, and the paste was then dried at 353 K for 12 h. The dried cake was crushed to a fine powder, moulded into cylindrical pellets, aged at 353 K for 24 h and then sintered at 1668 K for 18 h.

The magnesium aluminates made from magnesium acetate, magnesium nitrate, magnesium carbonate and hydrated magnesium oxide have been designated as MgA-A, MgA-N, MgA-C and MgA-H, respectively.

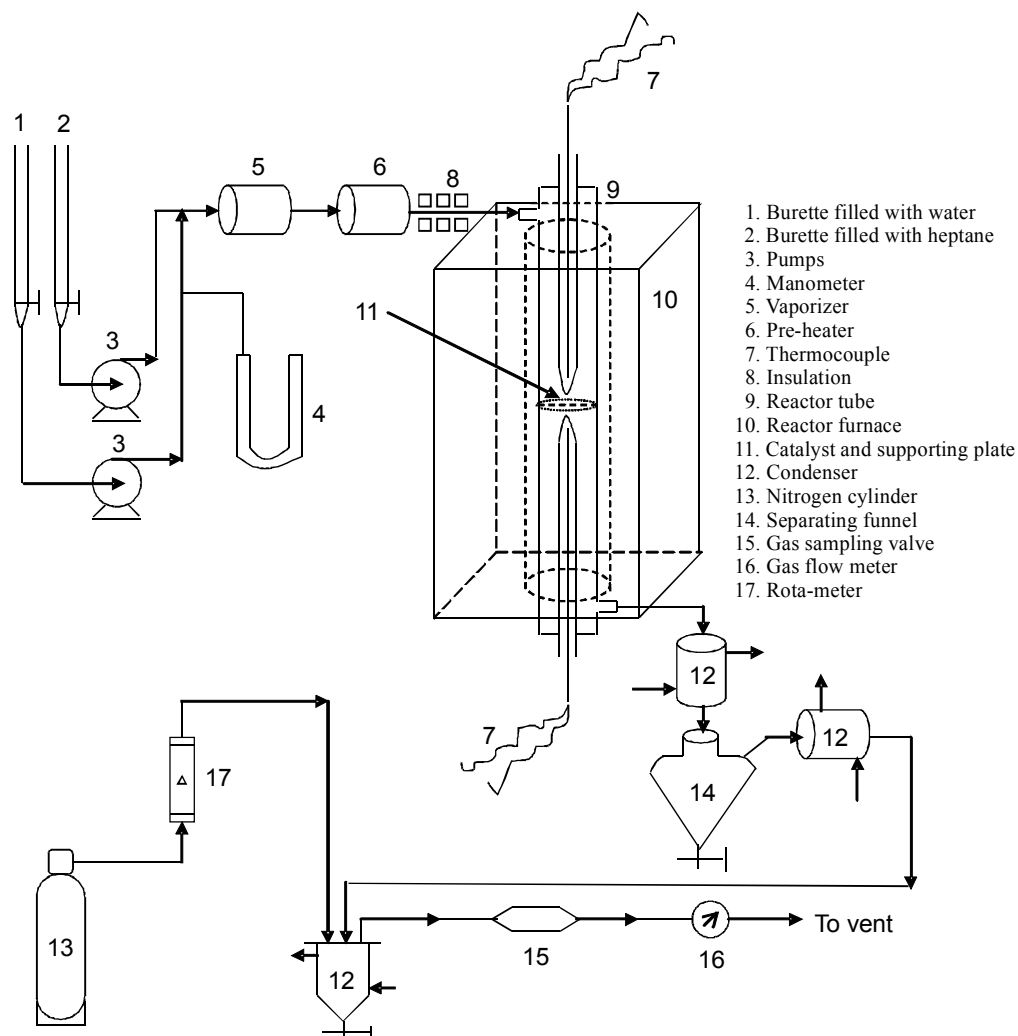
### **Catalyst characterization**

The catalysts were characterized by X-ray diffraction, surface area and pore volume measurement,  $\text{CO}_2$  chemisorption and weight loss during reduction. The X-ray diffraction spectra were obtained on a Reich Seifert Iso Debye Flex 2002 X-ray power diffractometer using monochromated  $\text{Cu-K}\alpha$  radiation. The surface area of the fresh catalysts was measured using the dynamic pulsing technique on a Micromeritics Pulse Chemisorb 2700 unit. The single-point BET method with nitrogen (30 mol%, balance helium) as the adsorbate was used. The pore volume was estimated by measuring the weight change when the dried catalyst was immersed in water. The relative surface basicity of each catalyst was determined by measuring the amount of  $\text{CO}_2$  chemisorbed at 323 K. Choudhary and Pandit<sup>11</sup> have discussed the determination of surface basicity and base strength distribution using stepwise thermal desorption (STD) of  $\text{CO}_2$ . Due to experimental limitations, STD could not be used and the relative total surface basicity was estimated by chemisorption of  $\text{CO}_2$ , using Micromeritics Pulse Chemisorb 2700 unit. The catalyst sample (~2.5 g) was first heated to 773 K in a flow of helium (30 mL/min) and kept at this temperature for 15 min for degasification. The sample was then cooled to 323 K and injected with pulses of  $\text{CO}_2$  using a fixed volume loop (0.05 mL) until saturation was obtained. The weight loss during reduction was determined using a thermogravimetric analyzer (Model TG 722, Harrop Industries, USA). The catalyst sample (~100 mg) was reduced in a flow of hydrogen (20 mL/min). The sample was heated from room temperature to 423 K, maintained at 423 K for 1 h for removal of any moisture, and then heated to 1073 K. The heating rate was 10 K/min.

## Catalytic test

### Experimental apparatus

The activities of the prepared catalysts were tested for the steam pyrolysis of n-heptane. The pyrolysis runs were conducted in an annular fixed-bed reactor. A schematic diagram of the experimental set-up is shown in Fig. 1.



**Fig. 1: Schematic diagram of the experimental setup**

n-Heptane (GR, Loba Chemie Pvt. Ltd., Bombay; 99.5%) and distilled water were taken in separate burettes and pumped by reciprocating pumps (Model RHSY, FMI, USA) to

a vaporizer. The flow rates of pumps could be varied from 0 to 60 cc/min. The temperature of the vaporizer was kept at approximately 573 K. In the vaporizer, the liquid heptane and water were vaporized and mixed at the outlet of the vaporizer. The mixed stream was then passed through a preheater where it was heated to approximately 773 K. The heated stream then entered the reactor through a well insulated connecting stainless steel tube (o.d.: 6 mm).

The reactor used was a 800 mm, stainless steel tube (i.d.: 19 mm; o.d.: 25 mm). The axial temperature profile in the reactor was measured using two thermowells (o.d.: 6 mm). One thermowell was attached to the top of the reactor, whereas the other was inserted from the reactor exit. A circular plate (dia.: 18 mm) containing twenty 1 mm holes was attached in the center of the reactor and served as the catalyst support plate. The reactor was heated in a three-zone furnace. The power was supplied to the three zones through on-off controllers (Blue Bell, Kanpur, India) whose set points were kept fixed to maintain the same temperature profile for all the runs.

The reactor effluent was quenched by passing it through three condensers connected in series. In the first condenser, recirculating water at room temperature was used as the coolant. The other two condensers were kept at 265 K by passing a mixture of glycerol-water using a refrigerated circulator (Model F-20HC, Julabo, Seelbach, Germany). The uncondensed gases were mixed with a metered flow of nitrogen. The flow rate of nitrogen was controlled using a mass flow controller (Model 8270, Matheson, USA).

Nitrogen was mixed with the effluent gas because it was used as the internal standard in the chromatographic analysis of the gaseous products. Most of the steam condensed in the first condenser and was collected in the glass separating funnel placed between the first and second condensers. The condensed hydrocarbon liquid was collected from the third condenser. The outlet gas along with nitrogen was then routed through one of the two sampling valves arranged in parallel. The effluent gas sample was trapped in one of the sampling valves, while another one was kept open to allow the gas to pass through a gas flowmeter and finally vented to the atmosphere.

### **Experimental procedure**

Both catalytic and noncatalytic runs were conducted for the steam pyrolysis of n-heptane. For the catalytic runs, the catalyst pellets were crushed, sieved and the  $3.0 \pm 0.5$  mm fraction was used. For the sake of comparison, noncatalytic pyrolysis runs were conducted at identical conditions. A run was started by heating the vaporizer, preheater and the reactor. The temperatures in the vaporizer and the preheater were maintained at 573 K and 773 K, respectively. For most of the runs, the catalytic zone temperature was 1023 K.

When the reactor temperature had stabilized to the desired value, water containing 100 ppm DMSO was fed to the reactor at a flow rate of 2.5 mL/min. DMSO was added in order to passivate the reactor walls and minimize the formation of carbon oxides. After 1 h of water feeding, n-heptane was fed at a flow rate of 1.5 mL/min to the system. The temperature initially decreased by 15–20 K but gradually stabilized after 30 minutes. This was due to the endothermic nature of the reaction. Water and liquid hydrocarbons were collected after each hour and the gas flow rate was also measured. The non-condensable gases containing mainly C<sub>1</sub> to C<sub>4</sub>, CO and CO<sub>2</sub> gases were trapped in sampling valves and analyzed by chromatography every hour. The condensed hydrocarbon products were analyzed on a capillary column. The run time was usually 3 h. The axial temperature profile was measured for each run. At the completion of the run, the heptane feeding was first stopped and the reactor further flushed with steam for one hour. After steam flushing, the reactor was allowed to cool down to room temperature. The reactor was then taken out of the furnace and the used catalyst collected and stored for subsequent measurement of coke deposition. The weight percent of coke deposited was found by taking the used catalyst from a run and then heating it in air at 1023 K for 12 h for complete oxidation of the coke. The weight difference between the used and the regenerated catalyst gave the weight percent of coke deposited.

### **Gaseous product analysis**

The non-condensable gases were analyzed by gas chromatography using three columns viz. Carbosphere, Durapak and Porapak Q. The analysis was done on two gas chromatographs. A Carbosphere column (dia.: 3.0 mm, length: 1.83 m) was used to separate nitrogen, carbon monoxide, methane and carbon dioxide using a thermal conductivity detector (TCD) on a CIC chromatograph (Model 85 PRO, Chromatograph Instrument Co., Baroda). Hydrogen was used as the carrier gas and its flow rate was 30 mL/min. The oven, injector and detector were maintained at 333 K, 393 K and 333 K, respectively. The bridge current was 100 mA. An electronic integrator (Model 3390A, Hewlett-Packard, USA) was used to record the peak areas. The second chromatograph (Model 5700, AIMIL-NUCON) was equipped with flame ionization detector (FID), and fitted with two columns, viz. Durapak (dia.: 3.0 mm, length: 3.0 m) and Porapak Q (dia.: 3.0 mm, length: 1.83 m). The hydrocarbon gases were separated in the Durapak column. The oven, injector and detector temperatures were 328 K, 343 K and 373 K, respectively. Nitrogen at a flow rate of 30 mL/min was used as the carrier gas. The peak areas were recorded by another electronic integrator (Model HP 3395, Hewlett Packard, USA). Since the separation of ethane and ethylene was not possible on the Durapak column, a Porapak Q column was used. The separation conditions for this column were the same as that for the Durapak column.

The flow rates of the gaseous products were calculated using flow rate of nitrogen, which was used as the internal standard. From the separation on the Carbosphere column, the peak area ratios of carbon monoxide, carbon dioxide and methane to nitrogen were calculated. Knowing the calibration factors on the Carbosphere column, the flow rates of methane, carbon monoxide and carbon dioxide in the product gases were found. Methane was then taken as a secondary standard to evaluate the flow rates of hydrocarbon gases from the peak area ratios determined on the Durapak and Porapak Q columns.

### **Liquid product analysis**

The liquid products collected from the reactor effluent were analyzed using a capillary column (Petrocol DH column) using an FID in a NUCON 5765 gas chromatograph. The capillary column was 0.25 mm in diameter and 100 m long. Nitrogen at 30 mL/min was used as the carrier gas. Air flow was maintained at a constant pressure of 1 kg/cm<sup>2</sup>. Flow rate of nitrogen in the capillary column was 1.5 mL/min and the split ratio was 1 : 50.

For analysis, the oven temperature was kept at 333 K for 15 minutes and then increased to a final temperature of 373 K at a rate of 2 K/min. The injector and the detector temperatures were 423 K and 493 K, respectively. 0.5 g of 2-2-4-trimethylpentane (iso-octane) was added to 1 g of the hydrocarbon liquid and 0.5  $\mu$ L of this mixture was injected in the capillary column. Iso-octane served as the internal standard. The peaks were recorded on a HP 3395 electronic integrator.

## **RESULTS AND DISCUSSION**

### **Physico-chemical properties of the catalysts**

The various properties of the four catalysts studied are summarized in Table 1. For all the four catalysts, the only crystalline phase present was MgO.Al<sub>2</sub>O<sub>3</sub>. The 'd' values of all the catalysts were in good agreement with the standard 'd' values.

Due to the high sintering temperature (1668 K), the surface areas of all the catalysts were low, and ranged between 0.94 to 1.38 m<sup>2</sup>/g. MgA-A had the highest surface area whereas the surface area of MgA-H was the lowest. Lemonidou and Vasolos<sup>5</sup> reported a surface area of 1.9 m<sup>2</sup>/g for MgO.Al<sub>2</sub>O<sub>3</sub> prepared by sintering at 1573 K. The trend in pore volumes and surface areas was similar.

As shown in Table 1, the weight loss during reduction for the different catalysts varied between 0.38 and 1.27%. For all the catalysts, most of the weight loss occurred

between 453 and 593 K. Out of all the catalysts, the weight loss for MgA-A was the highest. In comparison, the weight loss during reduction for calcium aluminate was reported to be 1.45 %<sup>5</sup>.

The amount of CO<sub>2</sub> chemisorbed at 323 K varied between 0.9 to 1.1 μmol/g (Table 1). The basicity of MgA-N was approximately 80% of that of MgA-A and MgA-H. For comparison, the chemisorption of CO<sub>2</sub> on MgO prepared from the different salts was also measured. The variation of the basicity of the differed magnesium aluminates followed the same trend as the basicity of the MgO precursors.

**Table 1: Physico-chemical properties of magnesium aluminates**

Property	Catalyst			
	MgA-A	MgA-N	MgA-C	MgA-H
Crystalline phase	MgO.Al <sub>2</sub> O <sub>3</sub>	MgO.Al <sub>2</sub> O <sub>3</sub>	MgO.Al <sub>2</sub> O <sub>3</sub>	MgO.Al <sub>2</sub> O <sub>3</sub>
Surface area, m <sup>2</sup> /g	1.38	1.06	1.24	0.94
Pore volume, cc/g	0.28	0.22	0.23	0.19
Wt. loss during reduction, %	1.27	0.74	0.38	0.38
CO <sub>2</sub> chemisorbed at 323 K, μmol/g	1.1	0.9	1.0	1.1

### Performance of the catalysts

All catalyst samples were tested at identical conditions. The operating conditions for the pyrolysis runs were: temperature, 1023 K; n-heptane flow rate, 1.0 g/min; steam flow rate, 2.5 g/min; mass of catalyst, 3.0 g. The catalyst to feed ratio was kept fixed at 175 (kg cat) (s)/(kg n-heptane). n-Heptane was of 99.5% purity and was used without further purification. To passivate the reactor walls, the water used for steam generation contained 100 ppm dimethyl sulphoxide. Although the tubular reactor had significant axial temperature gradients, there was an isothermal zone in the central portion of the reactor where the catalyst was placed. For the sake of comparison, noncatalytic pyrolysis runs were also conducted at identical conditions.

The conversion and product yields obtained with the different catalysts as well as without catalyst are shown in Table 2. At these conditions, the conversion of n-heptane



during noncatalytic pyrolysis was 67.4%, which is in good agreement with the conversion of 68.0% reported earlier<sup>13</sup> at identical conditions. As expected, methane, ethylene and propylene were the main products and constituted approximately 80 wt. of the total products. The hydrocarbon product selectivities (moles product/mole cracked, were in good agreement with published values<sup>8,13</sup>. Depending on the temperature, space time, material of construction of the reactor and the sulphur content of feed, different investigators have obtained either very little or significant amounts of carbon oxides during noncatalytic pyrolysis of n-heptane. Taralas et al.<sup>8</sup> reported that the carbon oxides increased from 0 at 973 K to 117 moles/100 moles of n-heptane cracked at 1023 K and a conversion of 55.7%. Similarly, Bajus et al.<sup>14</sup>, who did not add any sulphur to the feed, also obtained significant amounts of carbon oxides in the effluents. In this study, due to addition of dimethyl sulphoxide, which passivated the reactor walls, the selectivity of CO and CO<sub>2</sub> during noncatalytic pyrolysis were only 3.2 and 4.4 moles per 100 moles of n-heptane cracked, respectively. During noncatalytic pyrolysis, carbon oxides are mainly produced by the reforming of hydrocarbons and to a minor extent by the reaction of steam with the deposited coke.

As can be seen from Table 2, the conversion of n-heptane increased significantly in the presence of all the catalysts. Both the cracked gas yields as well as the yield of carbon oxides were affected due to the presence of the catalyst. Highest conversion was obtained with MgA-A and MgA-H catalysts and significantly lower conversion with MgA-N. At these conditions, conversion increased by approximately 22% when MgA-A was used as the catalyst. In comparison, Taralas et al.<sup>8</sup> reported an increase of 31.2% in the overall n-heptane conversion using MgO as a catalyst. However, the time factors used by them were significantly higher (0.015-0.067 kg.h/m<sup>3</sup>) compared to 0.004 kg.h/m<sup>3</sup> used in this study. The trend in ethylene yields were similar to that of conversion i.e., higher is the conversion, higher was the ethylene yield. In contrast, the yield of propylene was highest with MgA-C and lowest with MgA-H.

The coke deposited on the catalyst was significantly different for the various catalysts (Table 2). The yield of CO<sub>2</sub> was not appreciably affected by the presence of a catalyst, whereas the yield of CO increased significantly. Moreover, the coke deposited on the catalyst was lower when the yield of CO was higher. This indicates that coke gasification contributes to the increase in the yield of carbon oxides during catalytic pyrolysis. In an earlier study<sup>12</sup>, unpromoted and potassium promoted calcium aluminates were tested as catalysts for n-heptane pyrolysis. For the same conditions as used in this study, the conversion of n-heptane with unpromoted calcium aluminate was 81.0% and the coke deposited on the catalyst after 3 h was 3.8 wt.%. With calcium aluminate containing 6.4 wt.

potassium, the coke deposited after 3 h reduced to 0.6 wt.%. Thus, the gasification activity of the unpromoted magnesium aluminates is higher than even the potassium promoted calcium aluminates.

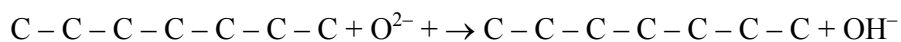
A comparison of product selectivities (moles product/mole n-heptane cracked) obtained in noncatalytic and catalytic pyrolysis showed that the product selectivities were not appreciably affected due to the presence of the magnesium aluminate. Similar results have also been reported for the catalytic pyrolysis of hydrocarbons using calcium aluminates<sup>1,5</sup>. This suggests that the catalysts increase the initiation of the free radicals, which is known to be the slowest step, and do not have any noticeable effect on the propagation and termination steps.

**Table 2: Conversion and product yields obtained with different catalysts**

Product yields, wt.% of feed	Without catalyst	With catalyst			
		MgA-A	MgA-N	MgA-C	MgA-H
Methane	8.2	8.8	8.7	9.1	9.4
Ethane	2.3	6.8	4.6	5.7	5.7
Ethylene	32.6	36.9	33.2	33.2	36.5
Propane	0.4	0.6	0.4	0.5	0.5
Propylene	12.4	13.9	13.0	14.2	12.7
1-Butene	2.3	3.7	3.7	4.8	3.4
1,3-Butadiene	3.3	3.6	3.2	4.7	4.1
C <sub>4+</sub>	5.6	4.1	2.5	3.9	5.9
Carbon monoxide	0.6	2.5	4.2	3.1	1.3
Carbon dioxide	1.3	2.0	1.6	1.5	1.6
Conversion, wt.% of feed	67.4	82.0	74.4	79.0	81.0
Coke deposited in 3 h, wt. % catalyst	-	0.42	0.23	0.32	0.58

The above results (Tables 1 and 2) show that the conversion and product yields obtained with the different catalysts did not correlate with either the surface area, pore volume or the weight loss during reduction. However, the cracking activity increased with

increasing basicity (as measured by CO<sub>2</sub> chemisorption). The most active catalyst (MgA-A) had the highest basicity whereas MgA-N, which had the lowest basicity was the least active. In this context, it should be noted that the basicity of MgO has also been reported to be strongly affected by the precursor used. Moreover, the differently coordinated O<sup>2-</sup> sites are most likely responsible for the basic sites of different strengths<sup>10</sup>. Although the nature of basic sites on magnesium aluminates is not precisely known, it is most likely due to the presence of oxygen ions on the surface. O<sup>2-</sup> can increase the initiation reaction as follows:



This cleavage of the C-H bond is known to be the slowest step in hydrocarbon pyrolysis. Mallens et al.<sup>15</sup> investigated the oxidative coupling of methane over MgO-based catalysts. Their data suggested that there were two types of surface lattice oxygen present, out of which one was active in methyl radical formation, and subsequently in the formation of ethane and ethylene, whereas the other lattice oxygen present was responsible for the direct conversion of carbon oxides. Our data suggest that in magnesium aluminates also, there may be two types of sites, one responsible for cracking and the other for coke gasification.

## CONCLUSIONS

The results of this study show that the source of magnesium oxide has a significant effect on the catalyst properties as well as on the activity of the catalyst for the cracking and gasification reactions. Compared to noncatalytic pyrolysis, the conversion and ethylene yields are enhanced in the presence of magnesium aluminates. The activity of the catalyst increase with an increase in the basicity of the catalyst.

### Nomenclature

d	Interplanar distance, Å
MgA-A	Magnesium aluminate catalyst prepared by using MgO obtained from magnesium acetate, and alumina
MgA-C	Magnesium aluminate catalyst prepared by using MgO obtained from magnesium carbonate, and alumina
MgA-H	Magnesium aluminate catalyst prepared by using MgO obtained from hydrated magnesium oxide, and alumina
MgA-N	Magnesium aluminate catalyst prepared by using MgO obtained from magnesium nitrate, and alumina

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