

# Oxidative dehydrogenation of propane with K-MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalysts

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**Abstract.** In this study, for the first time, MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalysts and their potassium-promoted forms were prepared and tested for oxidative dehydrogenation of propane. Catalysts were characterized with XRD, BET, NH<sub>3</sub>-TPD, TPR and XPS methods. Catalytic activity measurement was done with quartz microreactor between 450 and 550°C. It has been observed that the conversion of propane increased with temperature and total hydrocarbon selectivity increased with molybdenum oxide content. The acidity of catalysts decreased with potassium addition due to interaction with MoO<sub>3</sub> sites. For this reason total hydrocarbon selectivity highly increased.

**Keywords.** Selective oxidation; catalysts; propane; molybdenum oxide.

## 1. Introduction

Oxidative dehydrogenation [ODH] of lower alkanes has gained great importance for petroleum gas utilization in recent years.<sup>1–3</sup> In ODH of propane reaction, there are no equilibrium problems and one part of the process heat can be supplied by exothermic reactions. From thermodynamic point of view, up to 100% conversion is possible. Acidic catalytic active sites are necessary to activate propane. However, allylic C—H bond of propylene is weaker than the secondary C—H bond of propane, and propylene selectivity is the main problem at high propane conversion levels. This in turn causes a handicap for acidic catalytic surfaces necessary for propane activation, because propylene desorption from surface is not fast enough and even worse, it is adsorbed on other sites. Therefore, ODH of propane studies focus on the propane activation mechanism, the effect of oxygen type on the product distribution, and the effect of reaction conditions and catalyst compositions on the reaction mechanism.<sup>1,2</sup> In general, catalyst systems are composed mainly of supported molybdenum oxides, vanadium oxides and their multicomponent mixtures<sup>4–11</sup> for oxidative dehydrogenation of propane.

It has been shown that catalyst preparation methods and compositions strongly affect catalytic activity.<sup>12</sup> The synergistic effect between different phases due to preparation method affects the properties of catalyst for ODH. For example, the presence of excess MoO<sub>3</sub> on the surface of catalyst provides higher catalytic activity

in comparison to the absence of the MoO<sub>3</sub> phase on the same catalyst. Moreover type of MoO<sub>x</sub> species are determined by the surface molybdenum density as well as the interaction between active site and support. These properties also affect the product selectivity on the ODH of propane.<sup>12,13</sup>

In this study the preparation and testing of K-MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> as novel catalysts were aimed for ODH of propane.

## 2. Experimental

### 2.1 Catalyst preparation

Catalysts with 5, 10, 15, 20% (wt) MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> were prepared by impregnation method. Ammonium heptamolybdate (Merck), dissolved in water and MgAl<sub>2</sub>O<sub>4</sub> powder added to this solution. Mixture was heated at 70°C for 3 h to give slurry phase. Samples were dried at 120°C overnight, then calcined at 550°C for 3 h. 3% potassium including catalyst were prepared with KNO<sub>3</sub> impregnation after ammonium heptamolybdate incorporation.

### 2.2 Catalysts characterization

Nitrogen physisorption measurements were carried out at –196°C with 200 mg samples by Quantachrome Nova after high-vacuum degassing of the catalysts at 300°C. XRD results were obtained from Siemens type diffractometer by using Cu K $\alpha$  radiation ( $\lambda = 1.5404 \text{ \AA}$ ). X-Ray Photoelectron Spectroscopy (XPS)

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measurements were done with Cratos XPS in fixed transmission mode. Temperature-programmed reduction (TPR) experiments were carried out in CATLAB<sup>TM</sup> micro reaction system with 200 mg samples of 250–355 micron size placed in a quartz micro reactor under atmospheric pressure. Reactor was heated up to 900°C at a rate of 20°C/min under H<sub>2</sub>/N<sub>2</sub> flow of 20 mL/min with a content of 5% H<sub>2</sub>. Hydrogen was determined by an on-line HIDEN Mass spectrometer.

### 2.3 Catalytic measurements

ODH reactions were carried out in a fixed bed tubular quartz reactor. Propane (99.95%, Linde), oxygen (99.99%, Linde) and Nitrogen (99.99%, Linde) were fed at atmospheric pressure with the composition of 8:8:59, respectively, to provide a total flow rate of 75 mL/min. Catalysts of 250–355 micron size were diluted with quartz chips at a weight ratio of 1:1 to provide a 400 mg catalyst charge. The dead volume of the reactor was filled with quartz chips in order to avoid homogeneous reactions. Agilent on-line GC system with TCD and FID detectors, molecular sieve 5A column for N<sub>2</sub>, O<sub>2</sub> and CO, and Pora PLOT Q column for hydrocarbons and CO<sub>2</sub> were used for the analysis.

## 3. Results and Discussion

The XRD peaks of pure MgAl<sub>2</sub>O<sub>4</sub> and 15% MoO<sub>3</sub> loaded catalysts are shown in figure 1. As seen in the figure, 2-theta = 26° belongs to crystalline MoO<sub>3</sub>, JPDS (05-0508). No K<sub>2</sub>O peaks were observed with potassium addition (not shown). It means that potassium is homogeneously distributed on the catalyst surface.<sup>14</sup>

The surface area measurement results are seen in table 1. Pure MgAl<sub>2</sub>O<sub>4</sub> surface area is 68 m<sup>2</sup>/g (not shown). Surface area of samples decreased with loading of molybdenum oxide. When molybdenum oxide content increased from 10 to 20%, the surface area of samples decreased from 58.8 to 38.3 m<sup>2</sup>/g. In addition, potassium oxide addition slightly decreased the surface area. These results are expected because of the plugging effect of loading oxides.<sup>15</sup> High surface area mainly comes from nano and micro pores. Small pores are partially plugged with impregnated oxides and surface area decreases.<sup>13</sup>

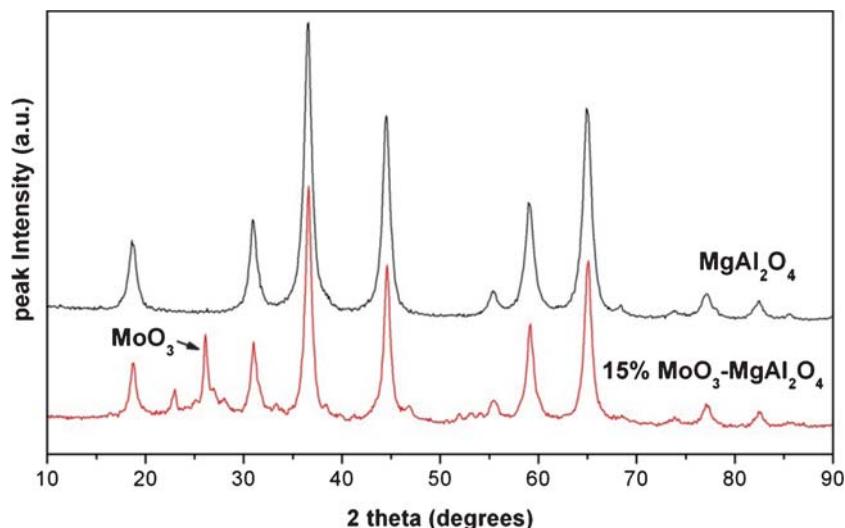
NH<sub>3</sub>-TPD were done for acidity measurements. This method is a highly powerful technique to observe surface acidity of this type of catalysts. As shown in table 2, the amount of desorbed NH<sub>3</sub> from 10% MoO<sub>3</sub> loaded catalyst is 33.6 μmol/g and the acidity value of 20% MoO<sub>3</sub> catalyst is 30.1 μmol/g. As it is observed

**Table 1.** Surface area results for some catalysts.

Catalyst	Surface area (m <sup>2</sup> /g)
10% MoO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>	58.6
20% MoO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>	38.3
K-10% MoO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>	56.1
K-20% MoO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>	35.7

**Table 2.** Acidity of catalysts.

Catalyst	Total acidity (μmol/g)
10% MoO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>	33.6
K-10% MoO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>	9.3
20% MoO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>	30.1
K-20% MoO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>	6.4



**Figure 1.** XRD pattern of 15% MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> and pure MgAl<sub>2</sub>O<sub>4</sub>.

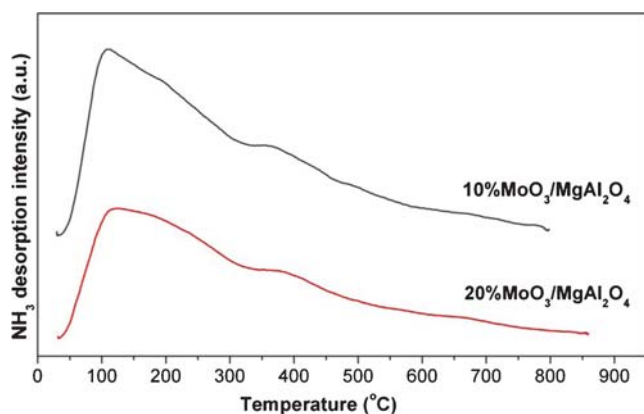
that the total acidity only slightly decreased from 10 to 20% MoO<sub>3</sub>. It is known that acidity comes from weak, mild and strongly adsorbed NH<sub>3</sub>.<sup>16</sup> Furthermore, a different type of surface molybdenum oxide domains can produce different acidity. Thus, the variation of molybdenum oxide domains is expected between 10 and 20% MoO<sub>3</sub> loading. As seen in table 2, total surface acidity of catalysts decreased with alkali (potassium) addition to 9.3 and 6.4 μmol/g for 10 to 20% MoO<sub>3</sub> loading, respectively. Since potassium addition increases the alkaline properties of the catalysts, total acidity decreases as well.

NH<sub>3</sub>-TPD curves of 10 and 20% MoO<sub>3</sub> loaded catalysts are seen in figure 2. As shown in these curves, there are two main peaks around 150 and 400°C, and there is a shoulder between these two temperatures. Those peaks and shoulders belong to weak, mild and strong acidity of catalysts, respectively. It is noted in NH<sub>3</sub>-TPD curves that shoulders around 260°C could indicate a higher fraction of mild acidic sites.<sup>16</sup> The effect of potassium loading to catalyst acidity are shown

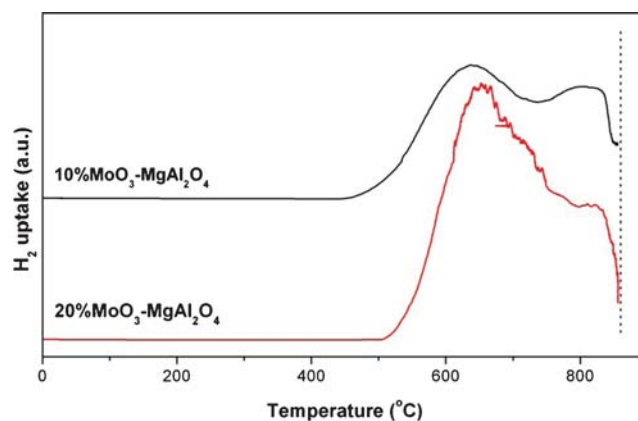
in figure 3. It can be seen that potassium addition decreases mainly the mild acidity. And these curves support the results that are reported in table 2.

Temperature programmed reduction (TPR) results of 10 and 20% MoO<sub>3</sub> loaded catalysts are seen in figure 4. The hydrogen uptake values of 10 and 20% MoO<sub>3</sub> catalysts are 1.69 mmol/g and 2.20 mmol/g, respectively. There are two main peaks and these two peaks around 650 and 815°C occurred due to Mo<sup>6+</sup> to Mo<sup>4+</sup> and Mo<sup>4+</sup> to lower valency states, respectively.<sup>17</sup> Results for potassium-added 10 and 20% MoO<sub>3</sub> catalysts are shown in figure 5. The hydrogen uptake values of potassium-added 10 and 20% MoO<sub>3</sub> catalysts are 1.73 mmol/g and 2.17 mmol/g, respectively. The first reduction peak of potassium-added 10 and 20% MoO<sub>3</sub> catalysts are slightly increased to 660 and 670°C, respectively. This result shows that potassium interacted with molybdenum oxide sites.<sup>18</sup>

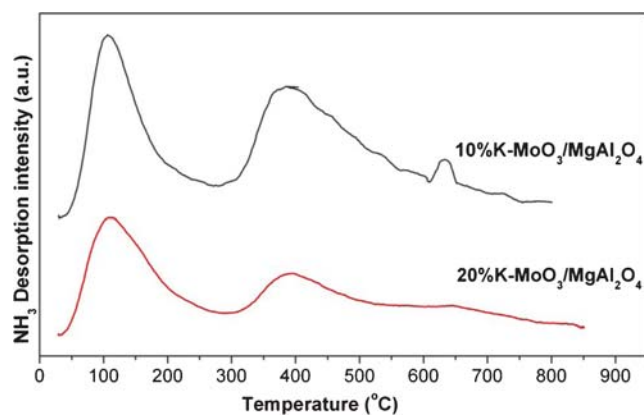
XPS spectra of the Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> energy regions were obtained for 10% MoO<sub>3</sub> and potassium-promoted 10% MoO<sub>3</sub> catalysts. As seen in figure 6, two



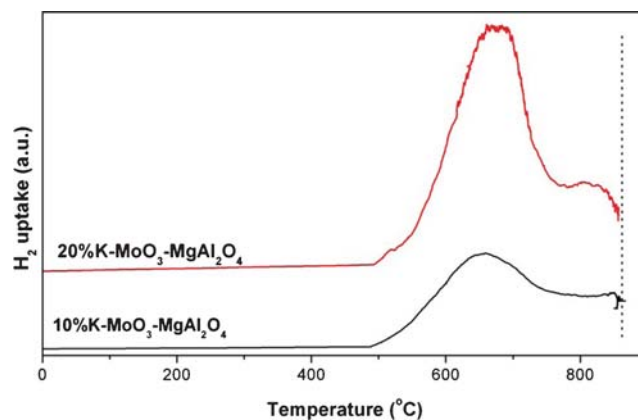
**Figure 2.** NH<sub>3</sub>-TPD thermal desorption of 10% MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> and 20% MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>.



**Figure 4.** TPR results 10%MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> and 20%MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>.

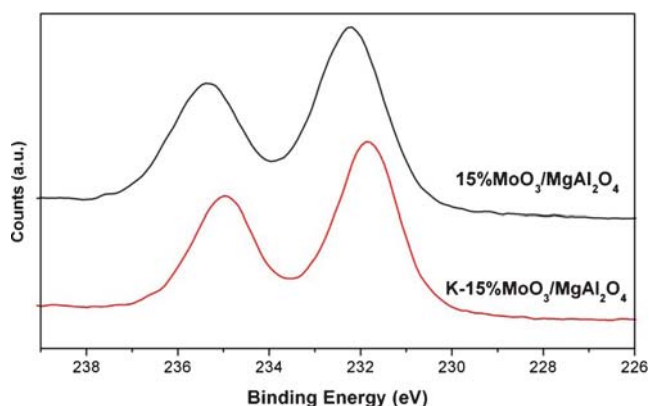


**Figure 3.** NH<sub>3</sub>-TPD thermal desorption of K-10% MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> and K-20% MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>.



**Figure 5.** TPR results K-10% MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> and K-20% MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>.

binding energies at 232.2 eV and 235.3 eV are characteristics of MoO<sub>3</sub>.<sup>17,18</sup> These two peaks shifted to 231.8 eV and 234.9 eV with potassium addition. These results



**Figure 6.** XPS spectra of 15% MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> and K-15% MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>.

show that potassium interacts with molybdenum oxide domains on the catalyst surface.<sup>14</sup>

Catalytic activity results of 5, 10, 15 and 20% MoO<sub>3</sub> loaded catalysts are shown in table 3. Experiments were run between 450 to 550°C. As seen in table 3, propane conversion increased with increasing reaction temperature. The main product of oxidative dehydrogenation of propane is propylene. Maximum selectivity to propylene was achieved as 65.2% with 20% MoO<sub>3</sub> catalyst. In this type of selective oxidation reaction, CO and CO<sub>2</sub> are formed as undesired products. For this reason, the total hydrocarbon selectivity is highly important. As seen in the table, 73% hydrocarbon selectivity were achieved with 20% MoO<sub>3</sub> loaded catalyst. Ethane, ethylene and methane are observed as secondary hydrocarbons, but main secondary hydrocarbon is methane in all the reactions.

Catalytic activity measurement results of potassium-added molybdenum oxide catalysts are shown in

**Table 3.** Catalytic activity results of MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalysts.

Catalyst	T (°C)	C (%)				S (%)			Hydrocarbon
		C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	
%5 MoO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>	450	1.0	30.1	8.7	<0.1	15.3	45.8	<0.1	54.1
	500	2.4	43.9	3.7	1.6	6.5	25.3	19.0	55.7
	550	5.1	58.5	1.7	3.0	3.2	10.2	23.3	66.4
%10 MoO <sub>3</sub> / MgAl <sub>2</sub> O <sub>4</sub>	450	1.2	18.7	6.9	<0.1	12.0	29.8	32.7	37.6
	500	1.9	39.9	4.7	<0.1	8.0	13.5	34.0	52.6
	550	3.6	58.2	2.5	1.9	4.4	20.2	12.8	67.0
%15 MoO <sub>3</sub> / MgAl <sub>2</sub> O <sub>4</sub>	450	1.2	15.9	7.0	<0.1	11.7	25.3	40.0	34.6
	500	1.9	32.7	4.5	<0.1	7.5	31.2	24.0	44.7
	550	2.8	60.9	3.0	1.1	5.2	18.2	11.6	70.2
%20 MoO <sub>3</sub> / MgAl <sub>2</sub> O <sub>4</sub>	450	1.4	20.2	5.8	<0.1	9.0	35.7	29.3	35.0
	500	2.0	44.5	4.2	<0.1	6.5	23.0	21.8	55.2
	550	3.7	65.2	2.4	1.4	4.0	17.4	9.7	73.0

C: conversion and S: selectivity

**Table 4.** Catalytic activity results of K-MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalysts.

Catalyst	T (°C)	C (%)				S (%)			Hydrocarbon
		C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	
K-%5 MoO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>	450	0.6	7.9	33.9	<0.1	58.2	<0.1	<0.1	>99.9
	500	0.3	21.2	29.2	<0.1	49.6	<0.1	<0.1	>99.9
	550	0.6	39.9	15.3	17.4	27.3	<0.1	<0.1	>99.9
K-%10 MoO <sub>3</sub> / MgAl <sub>2</sub> O <sub>4</sub>	450	1.4	<0.1	9.9	<0.1	19.8	27.9	42.4	29.7
	500	1.0	3.1	8.4	<0.1	14.4	<0.1	74.0	22.8
	550	0.3	45.5	17.9	9.9	26.7	<0.1	<0.1	>99.9
K-%15 MoO <sub>3</sub> / MgAl <sub>2</sub> O <sub>4</sub>	450	1.6	1.0	5.3	<0.1	9.0	25.1	59.6	15.3
	500	0.6	9.8	14.0	<0.1	23.8	<0.1	52.4	47.6
	550	1.2	16.9	7.2	3.0	13.1	25.2	34.5	40.2
K-%20 MoO <sub>3</sub> / MgAl <sub>2</sub> O <sub>4</sub>	450	1.0	2.4	8.3	<0.1	12.3	28.7	48.3	23.0
	500	1.2	6.6	7.1	<0.1	10.7	32.3	43.4	24.7
	550	1.6	17.7	5.7	2.6	9.7	35.3	29.1	35.7

C: conversion and S: selectivity

table 4. Alkali metal promotion slows down the reduction cycle of molybdenum oxide type catalysts.<sup>19</sup> Therefore, the decrease of undesired combustion products and increase in the amount of hydrocarbon selectivity are expected. As seen in the table, total hydrocarbon selectivity increased greatly almost up to 100% with potassium-promoted 5% MoO<sub>3</sub> catalyst. In particular, propylene is strongly adsorbed on catalyst acid sites and then it is converted to combustion products as CO and CO<sub>2</sub> due to its weaker allylic C-H bonds. It is known that alkali promotion decreases acidity of the catalyst and make easier desorption of hydrocarbons from the catalyst surface. Therefore, further combustion products are suppressed.<sup>14,18</sup>

#### 4. Conclusions

In this study for the first time, different amount of loaded MoO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalysts and their potassium-promoted forms were prepared and tested for oxidative dehydrogenation of propane. The conversion of propane increased with temperature and the total hydrocarbon selectivity increased with molybdenum oxide content. Potassium addition suppressed the acidity of catalysts due to interaction with MoO<sub>3</sub> sites. For this reason, total hydrocarbon selectivity highly increased. Further studies will be done with different support materials and alkali oxides.

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