

Article

Promoting Li/MgO Catalyst with Molybdenum Oxide for Oxidative Conversion of n-Hexane

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Abstract: In this work, molybdena-promoted Li/MgO is studied as a catalyst for the oxidative conversion of n-hexane. The structure of the catalysts is investigated with X-ray Diffraction (XRD) and Raman spectroscopy. The MoO₃/Li/MgO catalyst contains three types of molybdena-containing species, the presence of which depend on molybdena loading. At low Mo/Li ratios (i) isolated dispersed $[MoO_4]^{2-}$ anionic species are observed. At high Mo/Li ratios, the formation of crystalline lithium molybdate phases such as (ii) monomeric Li₂MoO₄ and tentatively (iii) polymeric Li₂Mo₄O₁₃ are concluded. The presence of these lithium molybdates diminishes the formation of Li₂CO₃ in the catalyst. Subsequently, the catalyst maintains high surface area and stability with time-on-stream during oxidative conversion. Molybdena loading as low as 0.5 wt % is sufficient to induce these improvements, maintaining the non-redox characteristics of the catalyst, whereas higher loadings enhance deep oxidation and oxidative dehydrogenation reactions. Promoting a Li/MgO catalyst with 0.5 wt % MoO₃ is thus efficient for selective conversion of n-hexane to alkenes, giving alkene yield up to 24% as well as good stability.

Keywords: Li/MgO; molybdenum oxide; oxidative dehydrogenation; oxidative cracking; n-hexane; Raman

1. Introduction

Catalytic oxidative conversion of alkanes to alkenes has gained interest over the years for on-purpose alkene production. The main challenge is that alkenes are highly reactive and susceptible to further oxidation in the presence of gaseous oxygen via adsorption on the catalyst surface. Therefore, to maintain high alkene yields in oxidative conditions, the use of basic catalysts is essential.

Li/MgO is a promising catalyst for the oxidative conversion (dehydrogenation/cracking) of lower alkanes to alkenes [1–12]. This catalyst has no formal redox character, i.e., Li⁺ and Mg²⁺ are not susceptible to oxidation state changes during the above reactions, and together with its inherent strong Brønsted basicity, it minimizes the re-adsorption and sequential combustion of formed alkenes [1–8]. Thus, the catalyst results in high selectivity to alkenes, which is highly desirable in the oxidative conversion of alkanes. This makes Li/MgO a better catalyst for oxidative reactions compared to acidic or redox-type catalysts, such as alumina or vanadia. It has been established through the work of Lunsford [13–18] on the oxidative coupling of methane that $[Li^+O^-]$ -type defect sites are responsible for catalytic activity. The nucleophilic [O⁻] site is a strong hydrogen abstractor and initiates alkane activation via homolytic scission of the C-H bond in the alkane forming a radical. However, contradicting this, more recently Schlögl and co-workers [19,20] concluded, supported by quantum chemical calculations, that $[Li^+O^-]$ is not the active site. Calculations on cluster models illustrated that both Li/MgO and MgO possess the same nature of active sites; i.e., low coordinated Mg²⁺O²⁻



sites $(Mg^{2+}LCO^{2-}LC)$ at steps and corners [19–22]. Thus, promotion with lithium does not introduce new active sites, but enhances the concentration of defect sites in MgO. In agreement, previous work from our lab suggests that lithium cations (Li⁺) and oxygen vacancies tend to segregate at steps and corners at the MgO surface, increasing the number of low coordinated Mg²⁺O²⁻ sites (Mg²⁺LCO²⁻LC), hence enhancing catalyst activity and selectivity [4,19,20,23]. The mechanism for oxidative conversion reaction over Li/MgO is analogous to that of the oxidative coupling of methane suggested by Schlögl and co-workers; i.e., heterolytic addition of the C–H bond of the alkane on the Mg²⁺O²⁻ pair in MgO, leading to a surface OH group and an alkyl radical [19,20]. The formed radical then undergoes a complex set of reactions in the gas phase in the presence of oxygen forming alkenes and alkanes, as well as combustion products, like H₂O and CO_x [1–11,24].

Recently, we reported [6,7] on the oxidative cracking of n-hexane over the Li/MgO catalyst. Our goal was to achieve higher selectivity to alkenes and lower combustion as compared to redox catalysts, which were previously attempted for the oxidative conversion of alkanes [25]. Indeed, Li/MgO resulted in lower combustion selectivity compared to catalysts containing oxides of facile redox properties, e.g., V_2O_5/MgO [25]. The low oxidation activity of the Li/MgO catalyst resulted in lower n-hexane conversions at the typical reaction temperatures (500–600 °C) studied [6]. Furthermore, Li/MgO catalysts deactivated during time-on-stream, which was attributed to the reaction of CO₂ with [Li⁺O⁻] catalytic sites and Li₂CO₃ formation [3,18,26]. Lunsford and co-workers confirmed that the presence of CO₂ increases the activation energy for methyl radical generation during the oxidative coupling of methane [18]. The same effect was reported by our group for the oxidative cracking of propane [2,3]. The product CO₂ interacts with [Li⁺O⁻] sites, forming an intermediate Li⁺CO₃⁻, which via further reaction with another [Li⁺O⁻] site is converted into the more stable Li₂CO₃ [18].

In order to improve both the activity and stability of Li/MgO, we promoted the catalyst with low amounts of oxides with redox properties [6]. Our goal was to add slight redox activity to the catalyst to enhance C–H bond scission and eventually n-hexane conversions. Of the different transition metal oxides attempted, molybdena-promoted Li/MgO showed the best alkene yields. Significantly, the presence of molybdena also prevented deactivation and catalyst stability was restored [6,7].

Supported molybdena catalysts have been often studied for the oxidative dehydrogenation of light alkanes, e.g., ethane, propane, and butane [27–38]. It has been suggested [31,32] that oxidation of the C–H bond in the alkane proceeds via a Mars-van-Krevelen redox mechanism with the participation of molybdena lattice oxygen, followed by re-oxidation with gas-phase oxygen.

Various molybdenum oxide systems have been reported, e.g., supported on MgO, ZrO_2 , Al_2O_3 , TiO_2 , and SiO_2 [32,35,36,39–43]. The presence of molybdena influences the physiochemical properties of the oxide support. In general, molybdena content, state of molybdena species on the surface of the support, and calcination temperature influence both the textural and acidic properties of the support. For example, in alumina-supported molybdena, in addition to Lewis acid sites, Brønsted acid sites are detected, the concentration of which depends on molybdena loading and calcination temperature [44]. In zirconia-supported molybdena, the increase in acidity with an increase in molybdena loading is correlated to the formation of Mo–O–Zr surface species as precursors for crystalline $Zr(MoO_4)_2$ [45]. Moreover, molybdena enhances the surface area of zirconia through stabilizing the tetragonal zirconia phase [46,47].

Generally, the performance of molybdena-based catalysts is related to the extent of crystallinity and chemical structure of the oxidic molybdena species on the support, e.g., free MoO₃, monomeric MoO_4^{2-} or polymeric $Mo_6O_{19}^{2-}$, $Mo_7O_{24}^{-6}$ units [32,35,41]. Hence, structure-performance correlations for supported molybdena catalysts have been of continuous interest. Magnesium oxide-supported molybdena (MoO₃/MgO), in particular, is reported to be an efficient and selective catalyst for the oxidative dehydrogenation of C₃–C₄ alkanes to the corresponding alkenes [33,34]. The activity of the MoO₃/MgO for alkane activation depends on the molybdena loading [37,38]. In the oxidative dehydrogenation of propane over a MgMoO_x catalyst, for example, Yoon et al. [37,38] reported that optimal molybdena loadings are necessary to maintain high propane conversions. Mg_{0.95}MoO_x crystallites with a slight excess of molybdenum (Mg/Mo = 0.9–1.0) showed the highest activity for propane conversion (22% conversion at 515 °C). Above these optimal loadings oxidation activity became significant. The high oxidation activity in these catalysts is due to the facile redox properties of molybdena, where the cation easily undergoes a change in the oxidation state (e.g., Mo^{6+} to Mo^{4+}) [25].

In relation to the chemical structure of the molybdates on magnesium oxide, extensive literature has been published on the topic [39–43]. Bare and co-workers [41,42] reported that, in the case of MoO_3/MgO catalysts, the structure of molybdena species depends on the molybdenum coverage of the support. For sub-monolayer coverages, dispersed species are observed. These consist of highly distorted octahedral molybdena species, e.g., MoO_6 , at low molybdenum loadings and regular octahedrally-coordinated polymolybdate species, e.g., $[Mo_7O_{24}]^{6-}$, at high molybdenum loadings [41]. For coverages exceeding the monolayer, crystalline magnesium molybdate (MgMoO₄), in which molybdenum is tetrahedrally coordinated, is observed as the dominant species. Raman spectroscopic studies [39,40] showed that for magnesium oxide-supported catalysts, surface molybdena species are sensitive to hydration. Upon exposure to water, octahedrally-coordinated molybdena species transform to tetrahedrally-coordinated $MoO_4^{2^-}$ species.

In this work, we present a detailed study on the role of molybdena in improving the performance of Li/MgO. A detailed characterization of the $MoO_3/Li/MgO$ catalysts is presented in order to identify the chemical structure of the different molybdena species (MoO_x) present on surface of Li/MgO. Our objective is to determine the influence of different molybdena species on (i) n-hexane conversion, (ii) alkene versus combustion selectivity, and (iii) catalyst stability. This is expected to help establish guidelines for developing an optimal catalyst for the oxidative conversion of n-hexane.

2. Results

2.1. Catalytic Tests

Figure 1 presents n-hexane conversions within 6 h of reaction time-on-stream. The Li/MgO catalyst suffered fast deactivation during the first hour of reaction. The 0.5MoO₃/Li/MgO catalyst resulted in similar initial n-hexane conversions to Li/MgO, however it exhibited better stability, hence significantly higher hexane conversions after 6 h time-on-stream. Both the 3.6MoO₃/Li/MgO and 7.1MoO₃/Li/MgO catalysts were very stable, but exhibited lower initial n-hexane conversions than the unpromoted Li/MgO.



Figure 1. n-Hexane conversion versus time. Reaction conditions: 100 mL/min, 10% n-hexane, 8% oxygen and balance helium, T = 575 °C. WHSV = 154 h^{-1} .

More specifically, Figure 2 presents n-hexane conversions as a function of Mo/Li ratio after 6 h of time-on-stream. The catalyst promoted with 0.5wt % molybdena (Mo/Li = 0.03) resulted in the highest activity, presenting significant improvement in activity compared to undoped Li/MgO.



Figure 2. n-Hexane conversion versus Mo/Li after 6 h of time-on-stream. Reaction conditions: 100 mL/min, 10% n-hexane, 8% oxygen and balance helium, T = 575 °C. WHSV = 154 h^{-1} .

The influence of varying loadings of molybdena on the performance of Li/MgO during the oxidative conversion of n-hexane at 575 °C is shown in Table 1. Initial conversions and corresponding product selectivities after 30 min time-on-stream are reported. It is important to note that product selectivities remained constant with time. 0.5MoO₃/Li/MgO showed similar conversion and selectivity to products as Li/MgO, however catalysts with higher molybdena loadings resulted in lower conversion and more combustion products.

	LiMgO	0.5MoO ₃ /Li/MgO	3.6MoO ₃ /Li/MgO	7.1MoO ₃ /Li/MgO
Conversion (mol %)				
n-Hexane	40.0	40.4	22.7	20.38
Oxygen	65.2	94.7	99.6	99.6
Selectivity based on C (mol %)				
CO	9.6	11.4	18.7	13.4
CO ₂	15.0	13.5	28.4	35.0
CH ₄	1.9	1.9	1.3	1.0
C ₂ –C ₅ alkanes	5.2	8.2	2.1	3.2
C_2H_4	23.2	22.6	11.4	7.2
C ₃ H ₆	25.9	24.2	12.4	11.3
$C_4 = (butenes)$	11.5	11.5	12.1	6.1
$C_5 = (pentenes)$	7.3	6.7	3.6	2.6
$C_6 = (hexenes)$	0.4	0.0	10.0	20.2

Table 1. Performance of various MoO₃/Li/MgO catalysts for the oxidative conversion of n-hexane. Reaction conditions: 100 mL/min, 10% n-hexane, 8% oxygen and balance helium, T = 575 °C. WHSV = 154 h^{-1} .

Moreover, in Figure 3 we compare selectivities to products at the same n-hexane conversion of ca. 10 mol %. The same n-hexane conversions were achieved through changing contact time with the catalyst. The $0.5MoO_3/Li/MgO$ catalyst showed a similar selectivity pattern to that of Li/MgO, while both the $3.6MoO_3/Li/MgO$ and $7.1MoO_3/Li/MgO$ catalysts resulted in the formation of more combustion products. Significant formation of C₆ alkene (hexene) was observed in the case of both the $3.6MoO_3/Li/MgO$ and $7.1MoO_3/Li/MgO$ catalysts. Oxygen conversion was almost same (~35 mol %) over both the Li/MgO and $0.5MoO_3/Li/MgO$ catalysts, while it increased to 43 mol % and 53 mol % over $3.6MoO_3/Li/MgO$ and $7.1MoO_3/Li/MgO$, respectively.

Figure 4 shows the selectivities to C_2 – C_4 alkenes as a function of n-hexane conversion. These results clearly indicate that the 0.5MoO₃/Li/MgO catalyst preserved the characteristics of the unpromoted catalyst and maintained the high alkene selectivity, even with increasing n-hexane conversion. However, both the 3.6MoO₃/Li/MgO and 7.1MoO₃/Li/MgO catalysts exhibited typical performance of redox catalysts, i.e., decreasing selectivity to alkenes with increasing conversion.



Figure 3. Selectivity to products based on carbon at an n-hexane conversion of 10 mol %. Oxygen conversions = 35 mol % (Li/MgO), 36 mol % ($0.5MoO_3/Li/MgO$), 43 mol % ($3.6MoO_3/Li/MgO$), and 53 mol % ($7.1MoO_3/Li/MgO$). Reaction conditions: 100 mL/min total flow, 10% n-hexane, 8% oxygen and balance helium, T = 575 °C. WHSV = 154-385 h⁻¹.



Figure 4. Selectivity to C_2 – C_4 alkenes as function of n-hexane conversion. Reaction conditions: 100 mL/min, 10% n-hexane, 8% oxygen and balance helium, T = 575 °C, WHSV = 5–154 h⁻¹.

2.2. Surface Area and XRD

The characteristics of the studied catalysts are presented in Table 2. It was observed that Li/MgO suffered a dramatic decrease in surface area upon calcination at 600 °C (15 m²/g), while in the presence of molybdena, high surface areas (70–82 m²/g) were retained. In the case of MgO, the loss in surface area upon calcination at 600 °C was less severe. Nevertheless, promotion with \geq 3.3 wt % of MoO₃ resulted in even higher surface areas than the unpromoted sample calcined at 600 °C (148 m²/g). The MoO_x surface coverage (θ) of molybdena-promoted catalysts shown in Table 2 were calculated based on the surface area of each catalyst and using 22 Å² as the mean surface area occupied by one Mo⁶⁺ oxide unit (MoO₃) [5]. Values indicated sub-monolayer coverage for all samples studied.

Figure 5 presents the XRD patterns of the catalysts. All catalysts exhibited characteristic peaks for crystalline MgO. No XRD peaks corresponding to crystalline MgMoO₄ or MgMo₂O₇ phases were observed, which would be expected at 2theta values between 20–300 [38]. The absence of such peaks confirms that molybdena phases were finely dispersed and no crystalline phases were observed. Our results are in good agreement with literature findings; in supported molybdenum oxide systems with sub-monolayer coverages the presence of dispersed molybdena anionic species such as $MoO_4^{2^-}$, $Mo_6O_{19}^{2^-}$, and $Mo_7O_{24}^{6^-}$ are commonly reported [32,35,36,41].

In addition, no peaks corresponding to any crystalline Li phases, e.g., Li_2CO_3 , were observed in any molybdena-promoted catalysts. The observed shift in the MgO peak positions in the MoO_x-containing samples indicates the formation of solid solutions between MoO_x and Li/MgO. The observed shift was

stronger in the $0.5MoO_3/Li/MgO$ and $3.6MoO_3/Li/MgO$ samples than in $7.1MoO_3/Li/MgO$, suggesting that the formation of lithium molybdates is dominant in the latter. This was further investigated by characterization of the catalysts with Raman spectroscopy.

Catalyst	BET Surface Area (m ² /g)	MoO ₃ Loading (wt %)	θ ^c (%)	Mo/Li ^d	
Li/MgO ^a	106	-	-	-	
Li/MgO ^b	15	-	-	-	
0.5MoO ₃ /Li/MgO ^b	70	0.51	7	0.03	
3.6MoO ₃ /Li/MgO ^b	76	3.60	45	0.20	
7.1MoO ₃ /Li/MgO ^b	82	7.11	86	0.40	
MgO ^a	195	-	-	-	
MgO ^b	148	-	-	-	
0.5MoO ₃ /MgO ^b	144	0.53	3	-	
3.3MoO ₃ /MgO ^b	178	3.26	17	-	
7.9MoO ₃ /MgO ^b	189	7.94	42	-	

Table 2. Characteristics of the cataly

^a calcined at 500 °C; ^b calcined at 600 °C; ^c surface coverage of Li/MgO by MoO_x ; ^d Atomic ratio of molybdenum to Lithium.



Figure 5. XRD patterns of Li/MgO and MoO₃/Li/MgO catalysts.

Figure 6 presents the XRD pattern of an equimolar mixture of Li_2CO_3 and $(NH_4)_2MoO_4$ calcined at conditions similar to that during catalyst preparation (600 °C for 5 h). In the same figure, results are compared to the XRD measurements of the Li_2CO_3 , Li_2MoO_4 , and $Li_2Mo_4O_{13}$ reference compounds and show the characteristic peaks of Li_2MoO_4 and $Li_2Mo_4O_{13}$.



Figure 6. XRD pattern of an equimolar mixture of Li_2CO_3 and $(NH4)_2MoO_4$ calcined at 600 °C, in comparison with the XRD of the Li_2CO_3 , Li_2MoO_4 , and $Li_2Mo_4O_{13}$ reference compounds.

2.3. Temperature Programmed Desorption (TPD)

Figure 7 presents results of TPD experiments for both fresh (a) and used (b) catalysts. The TPD of Li/MgO exhibited a broad CO_2 desorption peak with a maximum at 860 °C, which is typical for Li₂CO₃ [18]. The presence of Li₂CO₃ (formed with CO₂ from ambient) is an inherent property of Li/MgO [4,26]. The TPD of the molybdena-promoted catalysts exhibited similar Li₂CO₃ peaks, however with lower intensity, decreasing with increasing molybdena loading. This confirms the gradual decrease in amounts of Li₂CO₃ in Li/MgO with increasing molybdena loading.



Figure 7. Temperature programmed desorption for (**a**) fresh Li/MgO and MoO₃/Li/MgO catalysts pretreated at 600 °C and (**b**) used Li/MgO and 0.5MoO₃/Li/MgO catalysts (signals are normalized to the BET surface area). For comparison TPD of MgO, fresh Li/MgO and MoO₃ are presented.

Similarly, the CO₂ desorption peak observed for the used $0.5MoO_3/Li/MgO$ is significantly smaller than that of used Li/MgO. The broad desorption peak observed between 600 and 700 °C in the used catalysts is attributed to the desorption of weakly adsorbed CO₂ on [Li⁺O⁻] sites forming [Li⁺CO₃⁻], as illustrated earlier by Lunsford [18].

2.4. Raman Spectra

All MoO₃/Li/MgO catalysts were characterized by Raman spectroscopy (Figure 8b). For better assignment of Raman bands, MgO promoted with comparable molybdena loadings was prepared and characterized (Figure 8a). At first, we assign the Raman bands of MoO₃/MgO. Figure 8a presents the Raman spectra of MoO₃/MgO samples. The Raman band at 800 cm⁻¹ was characteristic in all samples and also appeared in the Raman spectra of Li/MgO in (Figure 8b). This band was not observed in any of the Raman spectra of MgO reported in literature [48]. Thus, the presence of such a band in our catalysts should relate to the sol–gel synthesized MgO support. This band was used as an internal standard when comparing intensities of Raman bands corresponding to the presence of molybdena species.

Bare et al. studied the surface chemistry of magnesium oxide-supported molybdenum oxide [41]. They reported that the structure of the molybdate species on MgO support after calcination at 600 °C in dry air depends on the molybdenum loadings. Below 3.3 wt %, isolated distorted octahedrally-coordinated molybdate species are present, which upon exposure to water saturated air transform to tetrahedrally-coordinated species. Above 6.7 wt % molybdenum, octahedrally-coordinated polymolybdate species are formed. Only above 20 wt % molybdenum is bulk magnesium molybdate formed from the reaction of MoO₃ with MgO.



Figure 8. Raman spectra of (**a**) molybdenum oxide supported on MgO and (**b**) molybdenum oxide supported on Li/MgO as function of loading of molybdena.

The Raman spectra of our MoO₃/MgO catalysts show close resemblance to those of MoO₃/MgO calcined at 600 °C and exposed to water-saturated air, reported by Bare et al. (see Table 3) [41]. The Raman band 445 cm⁻¹ appearing in all MoO₃/MgO samples is a characteristic for the lattice vibration and Mg–O stretching vibration in Mg(OH)₂ [41]. The 0.5MoO₃/MgO exhibited a Raman band at 908 cm⁻¹, which, with increasing the molybdena amount, increased in intensity and shifted to 912 cm⁻¹ and 917 cm⁻¹ for 3.3MoO₃/MgO and 7.9MoO₃/MgO, respectively. Thus, in agreement with Bare and co-workers [41], we assigned the Raman bands at 912 cm⁻¹, 874 cm⁻¹, and 320 cm⁻¹ in the 3.3MoO₃/MgO and the bands at 917 cm⁻¹, 874 cm⁻¹, and 325 cm⁻¹ in the 7.9MoO₃/MgO to the symmetric, antisymmetric stretching, and bending modes, respectively, of terminal Mo–O_t in tetrahedrally-coordinated isolated MoO₄²⁻ species. These assignments are summarized in Table 3.

Mode Assignments	Compound	D (Raman Band Number		
		Keference	0.5MoO ₃ /MgO	3.3MoO ₃ /MgO	7.9MoO ₃ /MgO
lattice vibration	Mg(OH) ₂	Bare et al. [41]		275	275
Mo–Ot bending	[MoO ₄] ²⁻	Bare et al. [41]		320	325
Mg-O stretching	Mg(OH) ₂	Bare et al. [41]	445	445	445
Mo-O-Mg vibrations	Mo-O-Mg	Bare et al. [41]		813	813
Mo-O-Mg vibrations	Mo-O-Mg	Bare et al. [41]		860	860
Mo-Ot asym stretching	$[MoO_4]^{2-1}$	Bare et al. [41]		874	874
Mo–O _t sym stretching	$[MoO_4]^{2-}$	Bare et al. [41]	909	912	917

Table 3. Raman bands of MoO₃/MgO catalysts.

Usually in MoO₃/MgO systems, a Raman band at 220 cm⁻¹ is characteristic of heptamolybdates [41,49]. The absence of this band in all the spectra (Figure 8a,b) indicates the absence of well-defined polymolybdate species in our systems. In the Raman spectra of 4.5–8.9 wt % molybdenum supported on MgO, calcined at 600 °C in dry air, Bare and co-workers [41] attributed Raman bands at 807 cm⁻¹ and 860 cm⁻¹ to Mo–O–Mg vibrations. The Raman band in our case at 813 cm⁻¹ and the shoulder at 860 cm⁻¹ in both 3.3MoO₃/MgO and 7.9MoO₃/MgO (Figure 8a) is therefore probably due to Mo–O–Mg vibration of Mo–O–Mg surface species.

Now, we study the Raman spectra of the molybdena-promoted Li/MgO catalysts (Figure 8b). The Raman bands 122 cm⁻¹, 155 cm⁻¹, 193 cm⁻¹ appearing in Li/MgO are characteristic for lattice vibrations in Li₂CO₃ [50,51]. Raman spectra of the molybdenum-containing catalysts showed significantly lower amounts of Li₂CO₃. These results are consistent with results obtained via

temperature-programmed desorption of CO_2 (Figure 7a), and confirm the role of molybdena in lowering the amount of Li_2CO_3 in Li/MgO.

Upon the promotion of Li/MgO with 0.5 wt % MoO₃, Raman bands at 275 cm⁻¹, 445 cm⁻¹, and 909 cm⁻¹ were observed. The Raman bands at 275 cm⁻¹ and 445 cm⁻¹ correspond, similar to in MoO₃/MgO, to the lattice vibration and Mg–O stretching vibration in Mg(OH)₂, respectively [41]. Generally, the Raman spectra of MoO₃/Li/MgO catalysts showed close resemblance to those of the MoO₃/MgO samples. The 0.5MoO₃/Li/MgO catalyst exhibited a very weak Raman band at 909 cm⁻¹, the latter increased in intensity and shifted to 912 cm⁻¹ and 917cm⁻¹ (shoulder) for the 3.3MoO₃/MgO and 7.9MoO₃/MgO catalysts, respectively. Therefore, similar to in MoO₃/MgO, we assigned the Raman band 909cm⁻¹ in the 0.5MoO₃/Li/MgO catalyst, the bands at 320 cm⁻¹ and 920cm⁻¹ in the 3.6MoO₃/Li/MgO catalyst to the stretching modes of terminal Mo–O_t in tetrahedrally-coordinated hydrated MoO₄²⁻ species. No free MoO₃ phases were detected in any MoO₃/Li/MgO catalyst.

The catalyst with the highest MoO₃ loading, 7.1MoO₃/Li/MgO, however, showed additional Raman bands at 289 cm⁻¹, 309 cm⁻¹, 820 cm⁻¹, 846 cm⁻¹, 878 cm⁻¹, 891 cm⁻¹, and 904 cm⁻¹ (Figure 8b). These were absent in the corresponding 7.9MoO₃/MgO catalyst. To investigate the nature of these phases we subtracted the Raman spectrum of the 7.9MoO₃/MgO catalyst from the corresponding spectrum of the 7.3MoO₃/Li/MgO catalyst. Figure 9 shows the difference spectrum. The majority of the bands appearing in the difference spectrum of the 7.1MoO₃/Li/MgO catalyst (309 cm⁻¹, 321 cm⁻¹, 358 cm⁻¹, 820 cm⁻¹, 846 cm⁻¹, 878 cm⁻¹, 904 cm⁻¹) match those of Li₂MoO₄. The bands at 904 cm⁻¹, 820-878 cm⁻¹, and 309–358 cm⁻¹ correspond to the symmetric, antisymmetric stretching, and bending modes of the terminal Mo–O_t bond in Li₂MoO₄, respectively [52]. Thus, in the case of the 7.1MoO₃/Li/MgO catalyst, part of the molybdenum is present as tetrahedrally-coordinated in a Li₂MoO₄ phase.



Figure 9. Raman spectrum of Li₂MoO₄ and the subtracted spectrum of 7.1MoO₃/Li/MgO-7.9MoO₃/MgO.

Additionally, the difference spectrum shows two sharp Raman bands at 289 cm⁻¹ and 891 cm⁻¹. The quasi-binary phase diagram of Li₂O and MoO₃ reported in literature [53] shows that in MoO₃-rich conditions (MoO₃/Li₂O > 0.5) at T > 600 °C, the formation of Li₂Mo₄O₁₃ is favored. We also observed the formation of such species by XRD (Figure 6). We tentatively assign the Raman bands at 289 cm⁻¹ and 891 cm⁻¹ to the bending and symmetric stretching modes of the terminal Mo–O_t bond in a well-defined Li₂Mo₄O₁₃ phase, while other Raman bands expected for Li₂Mo₄O₁₃ (160–420 cm⁻¹,

420–746 cm⁻¹, and 845–991 cm⁻¹) [54] were not clearly detected. We hence suggest in catalysts with 7.1 wt % MoO₃ the possible presence of Li₂Mo₄O₁₃ polymolybdate species. Li₂Mo₄O₁₃ is reported in literature [55] to have a regular derivative structure of V₆O₁₃, in which Mo is octahedrally-coordinated. Table 4 summarizes the Raman bands and corresponding molybdena phases in molybdena-promoted Li/MgO.

Mode Assignments	Compound	Reference	Raman Band Number			
			0.5MoO ₃ /Li/MgO	3.6MoO ₃ /Li/MgO	7.1MoO ₃ /Li/MgO	
lattice vibration	Li ₂ CO ₃	G. Li et al. [51]	122	122	122	
lattice vibration	Li ₂ CO ₃	G. Li et al. [51]	155	155	155	
lattice vibration	Li ₂ CO ₄	G. Li et al. [51]	193	193	193	
lattice vibration	Mg(OH) ₂	Bare et al. [41]	275	275	-	
Mo–Ot bending	Li ₂ Mo ₄ O ₁₃	Wan et al. [54]	-	-	289	
Mo–Ot bending	Li ₂ MoO ₄	Erdöhelyi et al. [52]	-	-	309	
Mo–Ot bending	[MoO ₄] ²⁻	Bare et al. [41]	-	320	321	
Mo–Ot bending	Li2MoO4	Erdöhelyi et al. [52]	-		321	
Mg-O stretching	Mg(OH) ₂	Bare et al. [41]	445	445	445	
Mo-Ot asym stretching	Li ₂ MoO ₄	Erdöhelyi et al. [52]	-	-	820	
Mo-Ot asym stretching	Li ₂ MoO ₄	Erdöhelyi et al. [52]	-	-	846	
Mo-Ot asym stretching	Li ₂ MoO ₄	Erdöhelyi et al. [52]	-	-	878	
Mo-Ot sym stretching	Li2Mo4O13	Wan et al. [54]	-	-	891	
Mo-Ot sym stretching	Li ₂ MoO ₄	Erdöhelyi et al. [52]	-	-	904	
Mo-Ot sym stretching	$[MoO_4]^{2-}$	Bare et al. [41]	909	912	917	

Table 4. Raman bands of MoO₃/Li/MgO catalysts.

In conclusion, the molybdena-promoted Li/MgO catalyst contains three types of molybdate species, the formation of which depends on the molybdena loading. At low Mo/Li ratios, in both the $0.5MoO_3/Li/MgO$ and $3.6MoO_3/Li/MgO$ catalysts, isolated dispersed $[MoO_4]^{2-}$ anionic species were detected. At high Mo/Li ratios, in the $7.1MoO_3/Li/MgO$ catalyst, the formation of crystalline lithium molybdate phases such as (i) monomeric Li₂MoO₄, and tentatively, (ii) polymeric Li₂Mo₄O₁₃ were detected. These lithium molybdate phases were present at low concentrations, below the detection limit of XRD and their formation became significant with increasing Mo/Li atomic ratio.

3. Discussion

The results presented above indicate that the promotion of Li/MgO with sub monolayer coverages of molybdena introduces structural changes, which influence both physical properties and the performance of the catalyst in the oxidative conversion of n-hexane. XRD and Raman spectra confirmed the presence of well-dispersed molybdena species in addition to lithium molybdates at high Mo/Li ratios, influencing catalyst performance, as discussed below.

3.1. Textural Properties and Stability of the Catalyst

The presence of Li₂CO₃, as confirmed by TPD results (Figure 7a) and previously reported [2,3,18], is an inherent property of Li/MgO. Trionfetti et al. [4] reported that only ~40% of the lithium incorporates into the MgO lattice as $[Li^+O^-]$ sites during the sol–gel preparation of Li/MgO, whereas the rest stays as Li₂O which forms Li₂CO₃ via reaction with ambient CO₂. The presence of Li₂CO₃ leads to detrimental changes in surface area upon exposure of the catalyst to high temperatures, as observed from the BET results in Table 2. Molybdena-promoted Li/MgO catalysts, however, exhibit less presence of Li₂CO₃, clearly observed from the TPD and Raman results, and consequently maintain a higher surface area even after exposure to high temperature treatment (Table 2). Hence, we conclude that the presence of molybdena reduces the amount of Li₂CO₃ in Li/MgO.

We suggest that during catalyst calcination at 600 °C, MoO₃, formed as a result of the decomposition of ammonium molybdate, reacts with the Li₂CO₃ present in Li/MgO, forming lithium molybdate mixed oxide phases. Indeed, the XRD pattern (Figure 6) of an equimolar mixture of Li₂CO₃ and (NH₄)₂MoO₄ calcined at similar conditions during catalyst preparation (600 °C for 5 h) resulted in characteristic

peaks of Li₂MoO₄ and Li₂Mo₄O₁₃. The absence of characteristic peaks of MoO₃ confirms the reactivity of MoO₃ with Li₂CO₃ in the catalyst, leading to the formation of lithium molybdate phases [47]. In our catalysts, these molybdates, as detected by Raman in Figure 8b, were present as dispersed species at low Mo/Li ratios ($0.5MoO_3/Li/MgO$ and $3.6MoO_3/Li/MgO$) and well-defined crystalline Li₂MoO₄ and tentatively Li₂Mo₄O₁₃ at high Mo/Li ratios.

In addition to Li_2CO_3 , inherently present in the catalyst, Li_2CO_3 is formed during oxidative reaction from the reaction of the product CO_2 with $[Li^+O^-]$ sites of Li/MgO. The formation of Li_2CO_3 in Li/MgO during the catalytic reaction was confirmed by the TPD of the used catalyst in Figure 7b. Li_2CO_3 sinters the catalyst at reaction temperatures [56], and consequently, this leads to degradation of defect sites and loss of catalytic activity.

The promotion of Li/MgO with molybdena improves the stability of the catalyst during oxidative conversion; all MoO₃/Li/MgO catalysts maintained stability within 6 h of reaction time-on-stream (Figure 1). The stability of all molybdena-promoted catalysts is attributed to the presence of the various aforementioned molybdate phases, which increase the surface acidity of Li/MgO. This in turn plays a positive role in minimizing the extent of CO₂ adsorption on [Li⁺O⁻] sites of Li/MgO and the subsequent formation of Li₂CO₃. The TPD of the used $0.5MoO_3/Li/MgO$ catalyst (Figure 7b), for example, confirmed that the formation of Li₂CO₃ was clearly partly suppressed. With less Li₂CO₃ formation during catalytic reaction, the catalyst preserves its high surface area, and hence catalytic activity.

3.2. Activity and Selectivity

The 0.5MoO₃/Li/MgO catalyst exhibited similar initial n-hexane conversion to Li/MgO, while catalysts with higher molybdena loading (3.6 and 7.1MoO₃/Li/MgO) exhibited even lower n-hexane conversions than Li/MgO (Figure 1). Increase in molybdena loading led to a clear increase in selectivity to CO_x , accompanied with a significant decrease in selectivity to C_2 – C_4 alkenes. In addition, a noticeable formation of hexene in the case of both 3.6 and 7.1 MoO₃/Li/MgO catalysts was observed (Figure 3).

The product selectivity patterns observed over the molybdena-doped catalysts in Figure 3 suggest that three competing parallel reaction pathways exist: (1) surface-initiated gas-phase oxidative conversion of n-hexane, (2) oxidative dehydrogenation (ODH) of n-hexane, and (3) surface-enhanced deep oxidation.

Hereby, we briefly describe, based on previous literature findings, the mechanisms of the above-mentioned three reaction pathways and the significance of their occurrence at various Mo/Li ratios.

At low Mo/Li ratios, surface-initiated oxidative conversion of n-hexane was significant, leading to high selectivity to light alkenes. At these conditions dispersed molybena species were present, which did not contribute to catalytic activity. The conversion of n-hexane was initiated via heterolytic C–H bond scission and hexyl radical formation on the O^{2-} of low coordinated $Mg^{2+}_{LC}O^{2-}_{LC}$ sites, in analogy to the suggestion by Sclögl and co-workers [19,20]. It is well established in the oxidative conversion of alkanes over Li/MgO that alkane activation proceeds via surface radical initiation [2,15–20]. The alkyl radical formed would undergo a series of gas-phase reactions in the presence of molecular oxygen, leading to the observed product composition for Li/MgO and 0.5MoO₃/Li/MgO catalysts in Figure 3.

Adversely, high Mo/Li ratios led to the formation of crystalline Li_2MoO_4 and $Li_2Mo_4O_{13}$ phases which enhanced the oxidative dehydrogenation of n-hexane to hexene and deep oxidation reactions. The ODH reaction occurs through subsequent hydrogen abstraction from the n-hexane via O^{2-} of MoO_x [25,31,32]. This, in agreement with literature [38], was most significant in catalyst with 7.1 wt % MoO₃, in which the presence of crystalline Li_2MoO_4 and $Li_2Mo_4O_{13}$ were detected by Raman. In studies by Vrieland and Murchison [38] on the oxidative dehydrogenation of butane to butadiene over MoO₃/MgO, maximum activity was attributed to presence of crystalline MgMoO₄.

Deep oxidation reactions occur via adsorption and stabilization of intermediate carbocations/radicals on O^{2-} of MoO_x and their consequent combustion to CO_x in the presence

of molecular oxygen. Both ODH and deep oxidation reactions explain the altered product composition observed for both 3.6MoO₃/Li/MgO and 7.1MoO₃/Li/MgO catalysts in Figure 3.

In the ODH of light alkanes, ethane and propane, it is well established that reactions on molybdena follow the Mars-van-Krevelen redox mechanism; i.e., molybdenum is reduced via loss of lattice oxygen and is then re-oxidized via molecular oxygen [25,31,32]. Consequently, in our catalysts with high molybdena loadings, excessive redox reactions resulted in complete consumption of molecular oxygen, hence limiting the n-hexane conversion route via molecular oxygen and inhibiting the extent of gas-phase radical chain reactions. Therefore, although C–H bond scission from n-hexane and ODH activity increased with the increase in molybdena loading, overall n-hexane conversions remained lower than in Li/MgO and 0.5MoO₃/Li/MgO catalysts.

The performance of 0.5MoO₃/Li/MgO mimicked that of Li/MgO, with similar initial activity as well as selectivity (Figure 4); moreover, the catalyst preserved activity with time-on-stream. The optimal Mo/Li ratio (Figure 2) is thus essential in order to, on one hand, maintain the non-redox nature of Li/MgO, and hence the desired high selectivity to alkenes (Figures 3 and 4), and on the other hand, to stabilize the catalyst activity (Figure 1).

4. Materials and Methods

4.1. Materials

Mg(OCH₃)₂ (6–8 wt%) solution in methanol (Sigma-Aldrich, Darmstadt, Germany), methanol (Merck, Darmstadt, Germany), and LiNO₃ (assay \geq 99.99%, Sigma-Aldrich, Darmstadt, Germany) were used for preparation of MgO and Li/MgO catalysts. Ammonium molybdate (99.98%, Sigma-Aldrich, Darmstadt, Germany) was used as the MoO₃ precursor. Pure n-hexane (GC assay \geq 99.0%, Fluka, Honeywell, USA) was used for catalytic experiments. The reference compounds Li₂MoO₄ (assay \geq 99.99%, Sigma-Aldrich, Darmstadt, Germany), Li₂CO₃ (assay \geq 99.0%, Sigma-Aldrich, Darmstadt, Germany), MoO₃ (assay 99.99%, Sigma-Aldrich, Darmstadt, Germany), and (NH₄)₆Mo₇O₂₄ (assay 99.98%, Sigma-Aldrich, Darmstadt, Germany) were used as received.

4.2. Catalyst Preparation

The MgO and Li/MgO catalysts used in this study were prepared according to the method described in detail earlier [4,7]. A methanol solution containing Mg(OCH₃)₂ (0.4 M) was mixed at room temperature with another methanol solution containing water (0.8 M) to form a sol. For Li/MgO, the required amount of LiNO₃ was added to the solution to obtain ~1 wt % Li. The solution was allowed to stay for gelation for 24 h. The gel formed was dried at 50 °C in vacuum for 7 h, and calcined at 600 °C in a flowing air of 50 mL/min for 1 h with a heating rate of 5 °C/min. Modified MoO₃/Li/MgO catalysts were prepared by wet impregnation of the sol–gel synthesized Li/MgO (calcined at 500 °C) using an aqueous solution of the ammonium molybdate. These were then dried at 50 °C in vacuum for 7 h and calcined at 600 °C in a flowing air of 50 mL/min for 5 h with a heating rate of 5 °C/min. Similarly, MoO₃/MgO catalysts were prepared with wet impregnation of the sol–gel synthesized MgO. Molybdena-promoted samples are denoted as xMoO₃/Li/MgO and xMoO₃/MgO, where x is wt % of MoO₃. Table 1 presents the list of the catalysts prepared.

4.3. Catalyst Characterization

The Brunauer–Emmett–Teller (BET) surface area of the catalyst was determined with nitrogen physisorption using a Micro-metrics Tristar instrument (Micro-metrics, USA).

X-ray Diffraction (XRD) patterns were recorded with a Philips PW 1830 diffractometer (Philips, Netherlands) using Cu K α radiation, $\lambda = 0.1544$ nm. Spectra were registered in the 2 θ range of 35 to 50 with step size of 0.01 and integration time of 1 s per step. Elemental composition of the catalysts was determined with atomic absorption spectroscopy (AAS). Li content in all the catalysts was 0.86 wt %.

Mo loadings were determined with X-ray fluorescence spectroscopy (XRF), using Phillips PW 1480 spectrometer (Philips, Netherlands).

Temperature programmed desorption (TPD) experiments were performed to decompose the Li_2CO_3 inherently present in both fresh and used catalysts. A total of 100 mg of the catalyst was pretreated in O₂/He at 600 °C for one hour to decompose any MgCO₃ present. After cooling the catalyst to 100 °C in helium, TPD was conducted from 100 °C to 950 °C, with an increment of 10 °C/min, with helium flow of 10 mL/min as a carrier gas.

Raman spectral measurements were conducted with a SENTERRA instrument (Bruker Optics, Netherlands) equipped with a cooled charge-coupled device (CCD) detector (-60 °C). The samples were excited with a 785 nm red laser of 100 mW power. Spectra were recorded at room temperature from 100 to 1000 cm⁻¹, at a resolution of 3 cm⁻¹ and a 5 min integration time.

4.4. Catalytic Tests

The catalytic tests were carried out at atmospheric pressure and isothermal conditions in a fixed-bed reactor [6]. An alumina tube reactor of 4 mm internal diameter was used. Powder catalyst was pressed, crushed, and sieved to particle size of 0.4–0.6 mm before use. A total of 10–100 mg of catalyst sample (to obtain varying contact times) was diluted in quartz particles and placed in the isothermal region of the furnace (1 cm). An alumina rod of 3 mm internal diameter was placed right below the catalytic bed to reduce the post catalytic volume in order to minimize homogenous gas-phase reactions. A Chromel-Alumel thermocouple inside a quartz tube was inserted above the catalytic bed to record reaction temperature. The temperature of the furnace was controlled by a second thermocouple placed outside the reactor tube within the isothermal zone of the tubular furnace.

Reactions were studied at 575 °C. Feed (100 mL/min) consisted of 10 mol % of n-hexane vapor, 8 mol % of oxygen, and balance helium. Similar n-hexane conversions were achieved by varying the weight hourly space velocity (WHSV). Before each catalytic test, the catalysts were pretreated at 625 °C in 50% O₂/He (60 mL/min) for 1 h. For analysis of the product, samples of outlet gas stream were injected into two micro gas chromatographies (micro GCs) (Varian CP4900, Netherlands) every 30 min during a period of 6 h. The first micro GC was a quad system consisting of four channels for the separation of O₂, N₂, CH₄ CO, CO₂, H₂O, C₂–C₄ hydrocarbons (alkanes and alkenes). The second micro GC was a dual system consisting of two channels for the separation of He, H₂, and C₆–C₈ hydrocarbons (alkanes and alkenes).

n-Hexane conversions were calculated on carbon mol basis; i.e., $(C_6^{in} \text{ moles} - C_6^{out} \text{ moles}) / C_6^{in}$ moles × 100%. The carbon balance closed between 100% and 105%. Selectivity to individual products was also calculated based on the number of moles of carbon contained in the products, divided by the total number of moles of carbon in the product mixture excluding unconverted feed; i.e., $(n_iC_i / \sum n_iC_i) \times 100\%$

5. Conclusions

Doping of Li/MgO catalyst with molybdena improves the performance in oxidative conversion of n-hexane. Promotion of Li/MgO with molybdena loading as low as 0.5wt % is sufficient to bring considerable improvements in the stability of the catalyst. Moreover, the catalyst exhibits similar activity for n-hexane conversion and selectivity to alkenes as the unpromoted Li/MgO.

 $MoO_3/Li/MgO$ catalysts contain three types of molybdena-containing phases, the formation of which depends on MoO_x loading. At low Mo/Li ratios, isolated dispersed $[MoO_4]^{2-}$ anionic species are observed. At high Mo/Li ratios, the formation of crystalline lithium molybdate phases such as (i) monomeric Li_2MoO_4 , and (ii) polymeric $Li_2Mo_4O_{13}$ are concluded. The presence of these lithium molybdates diminishes the formation of Li_2CO_3 in the catalyst. Subsequently, the catalyst maintains high surface area and stability with time-on-stream during oxidative conversion.

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