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Selective Production of Propylene and 1-Butene from Ethylene by Catalytic Cascade Reactions

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TOC graphic



ABSTRACT: In this study we report that ethylene can be simultaneously and selectively converted into propylene and 1-butene through one-pot catalytic cascade reactions. In a single continuous flow reactor, and under identical mild conditions (60 °C, 3 MPa), without the use of co-catalyst, ethylene was first dimerized/isomerized over Ni-AlKIT-6 catalysts to form butenes, which reacted then with the excess of ethylene over ReO_x/Al₂O₃ to produce propylene and 1-butene with more than 86% total selectivity. The selectivity for 1-butene was 97.4% in the C4 fraction. The initial ethylene conversion was 73% and stabilized at 35% after 4 h on stream, with around 45% selectivity in propylene and 42% selectivity in 1-butene.

KEYWORDS: heterogeneous catalysis, oligomerization, metathesis, ethylene, propylene, 1butene

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With stricter environmental regulation and depletion of fossil feedstock, renewable resources attracted increased interest in recent research. Various new bio-based molecules were proposed for replacing the platform chemicals based on crude oil, but there are not yet well established processes for producing these chemicals at large scale.¹⁻³ As a result, in the short to mid-term, a much larger impact might be expected from the production of bio-based molecules with a structure identical to today's bulk chemicals. Among them, ethylene is one of the most promising bio-based chemicals, mainly because its high-volume production by bioethanol dehydration became economically feasible. Additionally, ethylene is a key intermediate for producing other major platform molecules like 1-butene and propylene.

The dimerization of ethylene to 1-butene is a well-known reaction. The commercial processes use organic solvents and homogeneous catalysts.^{4,5} The challenge is to obtain 1-butene in greener dimerization processes based on heterogeneous catalysis. Among the main solid catalysts studied, namely immobilized complexes on polymers and oxides,⁶⁻⁸ metal organic frameworks (MOFs) materials⁹⁻¹² and nickel supported on inorganic porous materials, the latter are the most promising.¹³ First, they are very robust and efficient catalysts for ethylene dimerization/oligomerization at temperatures lower than 150 °C.¹⁴⁻¹⁶ Moreover, unlike other catalysts, no activator or co-catalyst is required in this case. Despite these advantages, the main drawback associated with this method is that among the C4 isomers, 2-butenes predominate to 1-butene.

Propylene can be also produced from ethylene *via* well-establish technology, i.e. crossmetathesis with 2-butene.¹⁷⁻¹⁹ This reaction is activated by Re, Mo and W-based catalysts and needs an equimolecular ethylene-butenes proportion. The high growth rate in the demand for propylene during the past decade and the need to develop sustainable feedstocks stimulated the interest for the conversion of ethylene to propylene without any addition of other

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hydrocarbons. Two methods, based on acid catalysts (at high temperature) and multifunctional heterogeneous catalysts (at lower temperature) are investigated.

The conversion of ethylene to propylene (ETP) at temperatures higher than 450 °C is catalyzed by zeolites and SAPOs.²⁰⁻²² The negative aspect of the acid microporous catalysts in this process are their severe deactivation with time on stream and the low selectivity to propylene.

On the other hand, some multifunctional catalysts and strategies have been recently proposed for producing propylene in ETP processes through successive dimerization/metathesis reactions using only ethylene as a raw-material. Iwamoto,²³ Seidel-Morgenstern²⁴ and Hinrichsen²⁵ groups reported that Ni-MCM-41 and Ni-MCM-48 catalysts prepared by "template ion exchange" catalyzed the conversion of ethylene to propylene at temperature higher than 350 °C. Basset and co-workers²⁶ reported the direct transformation of ethylene to propylene over tungsten hydride supported on γ -alumina at 150 °C. Li et al.²⁷ reported that a dual site bimetallic catalyst, NiSO₄/Re₂O₇/ γ -Al₂O₃, catalyzed the direct conversion of ethylene to propylene at 50 °C, in a reactor operated in pulse mode. A multicomponent catalyst, namely NiO/Re₂O₇/B₂O₃-Al₂O₃ was also able to activate the ETP reaction at 80 °C.²⁸ Conditions of reaction for these studies and the main experimental results will be summarized below.

More recently, we have reported an original method for converting ethylene to propylene involving cascade oligomerization/isomerization/metathesis reactions over two robust, air stable, and highly active heterogeneous catalysts.^{29,30} In a single flow reactor and under identical conditions, ethylene was selectively dimerized/isomerized over Ni-AlSBA-15 or Ni-AlSiO₂ catalysts to form 2-butenes, which then reacted then with the excess of ethylene over Mo-based catalysts to produce propylene (Scheme 1).



Scheme 1. Conversion of ethylene to propylene in a cascade process

 At 80 °C and 3 MPa, the average conversion of ethylene was 40% leading to specific activities up to 48 mmol of propylene per gram of catalyst per hour, with a selectivity of 90% for propylene and butenes, but with a majority of 2-butenes (20% 1-C4 and 80% 2-C4). Herein we report on a new very efficient heterogeneous catalytic system associating Ni-AlKIT-6 and ReO_x/ γ -Al₂O₃, which is able to transform selectively ethylene into propylene and 1-butene. KIT-6 is an ideal support combining high surface area and large interconnected mesopores with homogeneous mesopore size distribution, which is key parameter for high mass transfer properties.^{31,32} ReO_x/ γ -Al₂O₃ is a well-known metathesis catalyst able to work at low temperature.^{18,33}

The dimerization/isomerization catalyst, Ni-AlKIT-6, was prepared by grafting a KIT-6 silica support (prepared according to our previous work³⁴) with sodium aluminate (NaAlO₂), followed by cation exchange, first with NH₄⁺ then with Ni²⁺. The exchanged sample was dried and then calcined for 5 h at 550 °C. Ni-AlKIT-6 had a Si/Al ratio of 7.0 and a Ni content of 1.9 wt%. The corresponding Ni/Al ratio is 0.2, indicating a partial exchange level of NH₄⁺ ions with Ni²⁺. As a consequence, Ni-AlKIT-6 contains both Ni²⁺ and Brønsted-type acidic sites. The metathesis catalyst, ReO_x/ γ -Al₂O₃ was prepared by incipient wetness impregnation using an aqueous solution of NH₄ReO₄ and a commercial γ -Al₂O₃. It contains 4.0 wt% Re (0.5 Re per nm²), corresponding to a ReO₄ loading of 5.4 wt%. After impregnation and drying, the catalyst was calcined in air at 550 °C for 8 h.

 The composition of the catalysts and their main textural characteristics are summarized in Table 1. Both catalysts have pores larger than 7 nm.

Table 1. Composition and texture of the catalysts

Catalyst	Si/Al mol mol ⁻¹	Me ^a wt%	D _P nm	V_P mL g ⁻¹	S_{BET} $m^2 g^{-1}$
Ni-AlKIT-6	7.0	1.9	7.0	0.71	390
ReO _x /γ-Al ₂ O ₃	-	4.0	13.5	0.73	260

^a Me = Ni or Re, BdB average pore diameter (D_P), total pore volume (V_P), BET specific surface area (S_{BET})

Nitrogen adsorption-desorption isotherm (Figure 1) of Ni-AlKIT-6 is of type IV, with a sharp capillary condensation step, characteristic of high-quality material with homogeneous mesopores. As previously reported,^{14,15} the large mesopores are very beneficial to the free diffusion of heavier oligomers/products inside the pore system, which results in a lower deactivation rate and higher activity in comparison to microporous materials as zeolites. ReO_x/ γ -Al₂O₃ exhibits mesopores with a large pore size distribution centered at 13 nm and a high surface area for alumina materials.



Figure 1. Nitrogen physisorption isotherms at -196 °C of (a) Ni-AlKIT-6 and (b) ReO_x/γ -Al₂O₃ catalysts

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Small-angle XRD pattern of Ni-AlKIT-6 (Figure S1) indicated the long range ordering of the mesopores and the bicontinous cubic *Ia3d* symmetry characteristic of KIT-6 topology.³⁵ ReO_x/ γ -Al₂O₃ was amorphous to XRD, confirming the absence of crystalline ReO_x. The ²⁷Al MAS NMR spectrum (Figure S2) confirmed the insertion of aluminum atoms as tetrahedrons in the silica network of KIT-6. Raman spectrum of the ReO_x/Al₂O₃ catalyst (Figure S3) indicated the presence of isolated ReO₄ species.^{36,37} TPR analysis of the Re-based catalyst revealed two peaks at 365 and 420 °C (Figure S4), which are assigned to reduction of Re⁷⁺ surface ions interacting with the support.³⁸ These peaks indicate that there are two different Re⁷⁺ species, although Raman spectroscopy detected only one monomeric tetrahedral species. The reduction signal at 365 °C is attributed to the isolated ReO₄ species, ³⁹

Before to perform the cascade reactions, the oligomerization reaction has been separately studied on Ni-AlKIT-6 catalyst. The ethylene oligomerization was performed in a stainless steel fixed bed reactor (i.d. 5 mm) using 0.2 g of Ni-based catalyst (0.15–0.25 mm sieve fraction). At 60 °C and 3 MPa, with a gas feed consisting of ethylene and nitrogen (5/1 vol/vol, 20 mL min⁻¹, WHSV = 7.5 h⁻¹), the reaction products were butenes (80%), hexenes (19%) and octenes (< 1%). In the C4 fraction, the only detected molecules were 1- and 2- butene. During 4 h on stream the molar ratio 1-C4/2-C4 varied from 35/65 to 47/53. The ethylene conversion decreased progressively from 47 to 27% (at 4 h on stream) and 16% (at 18 h on stream). The typical composition of C6 fraction was: 5% 1-C6, 40% 2-C6, 25% 3-C6, 25% 3-methyl-1-C5.

To produce propylene from ethylene oligomerization-metathesis reactions, according to Scheme 1, two consecutive catalyst beds consisting of Ni-AlKIT-6 (0.2 g) and ReO_x/γ -Al₂O₃ (0.5 g) were placed in the same reactor. Thus, the metathesis catalyst is in excess compared to

the oligomerization catalyst. The reaction was conducted at 60 °C, 3 MPa and with a gas flow rate of 20 mL min⁻¹ (ethylene/nitrogen : 5/1 vol/vol). The low temperature limits the formation of high molecular weight oligomers in the oligomerization step, and increases the conversion in the metathesis step. Figure 2 shows a typical chromatogram obtained during the reaction. The major products were propylene and butenes (selectivity up to 86%). Some pentenes and hexenes were also detected in low concentration (selectivity of 10-12%). The presence of small amount of C5 olefins indicate that ReO_x/γ -Al₂O₃ catalyzes also some metathesis reactions involving C6 olefins.



Figure 2. Typical chromatogram for ethylene conversion; all products are unsaturated hydrocarbons

The selectivity for 1-butene in the C4 fraction was remarkably high : 97.4% 1-C4, 1.9% 2-*cis*-C4 and 0.7% 2-*trans*-C4. This value exceeds the selectivities previously obtained with various solid catalysts (Table 2). It is comparable to the highest ethylene dimerization selectivity ever obtained over MOF catalysts, in the presence of co-catalyst, recently reported by Metzer et al.¹²

Catalyst	Me, wt%	T, °C	P, MPa	1-C4 selectivity, %	Ref
Ni-MCM-41	5.0	-15	3.0	93	40
Cr-Co-C	13.0 (Co), 5.0 (Cr)	80	3.1	93.6	41
Ni-MOF ^b	10.0	25	3.0	95	9
Ni-MOF ^c	1.0	25	5.0	96.2	12
$Ni-AlKIT-6+ReOx/\gamma-Al_2O_3$	1.9 (Ni), 4 (Re)	60	3.0	97.4	This study

Table 2. 1-Butene selectivity in ethylene dimerization over selected catalysts^a

^a 1-butene (%mol) among butenes; ^b co-catalyst Et₂AlCl ; ^c co-catalyst MAO

From a quantitative point of view, the process was also very efficient. The initial conversion of ethylene reached 73% and decreased progressively to stabilize around 35% after 4 h on stream (Figure 3).



Figure 3. Ethylene conversion (\Box), propylene (\circ) and 1-butene (Δ) selectivity (%mol) as a function of time at 60 °C.

Deactivation is a systematic well-known drawback for the metathesis catalysts, most probably due to the poisoning of the active centers by strongly adsorbed products. The initial selectivity in propylene and 1-butene were 60 and 30 mol%. These values vary with the time on stream (TOS), to stabilize at 45 and 42 mol%, respectively, after 4 h of reaction (Figure 3). The decrease of propylene and the increase of 1-butene are consistent with the oligomerization

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step results: 2-butene, responsible for propylene formation by metathesis, decreases from 65 to 53%, while 1-butene increases from 35 to 47%. The turnover frequency (TOF) values varied from 503 to 235 $\text{mol}_{C2H4} \text{ mol}_{Ni}^{-1} \text{ h}^{-1}$, and the turnover number (TON = TOF x TOS) after 4 h of reaction was more than 1200.

The direct conversion of ethylene into propylene, without addition of other hydrocarbons, has been investigated over various catalytic systems. The specific activity in propylene and 1butene obtained in the present study is compared with those reported in literature (Table 3). The specific activity in propylene and 1-butene are among the highest achieved in such a process. In addition, this process is the only one leading to almost pure 1-butene (more than 97% in the C4 fraction).

Catalysts	T, ℃	P,	C2 conv., ^a	C3, ^a	1-C4, ^a	Ref
		MPa	%	$\operatorname{mmol}_{\operatorname{C3}}$	mmol_{C4}	
				$g_{catal}^{-1} h^{-1}$	$g_{catal}^{-1} h^{-1}$	
Ni-MCM-41	400	0.1	68	3.1	2.8 ^d	23
Ni-AlMCM-41	400	0.1	75	1.1	0.1 ^e	24
Ni-MCM-48	350	0.1	48	0.8	0.1 ^d	25
W-H/ γ -Al ₂ O ₃	150	0.1	40-10 ^b	9.6-2 ^b	0.2 ^e	26
$NiSO_4/Re_2O_7/\gamma$ - Al_2O_3	50	0.1	60	12.6	4.5 ^d	27
$Pd/Re_2O_7\!/B_2O_3\text{-}Al_2O_3$	80	0.1	22	2.8	traces	28
$Ni\text{-}AlSBA\text{-}15 + MoO_3 \text{-}SiO_2 \text{-}Al_2O_3$	80	3.0	40	48.0	10.0 ^e	29
$Ni\text{-}AlSiO_2 + MoO_x/(Al)SiO_2$	80	3.0	41	28.0	5.1 ^e	30
Ni-AlKIT-6 + ReO _x /γ-Al ₂ O ₃	60	3.0	73-35 ^c	26.0-9.3 ^c	13.0-8.7 ^{c,f}	This study

Table 3. Direct conversion of ethylene into propylene with multifunctional catalysts

^a the highest values in each study; ^b 0.1-30 h on stream; ^c 0.3-4 h on stream (only ReO_x/γ -Al₂O₃ was considered as catalyst for this evaluation); ^d 1-butene represents about 30% among the C4 isomers; ^e 1-butene represents about 20% among the C4 isomers; ^f 1-butene represents > 97% among the C4 isomers

Accordingly to previous studies,^{15,16,29,30} the present catalytic behavior can be explained as follow. Two ethylene molecules coordinated to a nickel ion on Ni-AlKIT-6 react to form 1-butene, some of them migrates to an acid sites to isomerize into *cis/trans*-2-butene. Over the

second catalyst, ReO_x/γ -Al₂O₃, the cross-metathesis between the excess of ethylene and butenes occurs (according to Scheme 1). The couple ethylene/(*cis/trans*-2-butene) gives propylene (Eq. 1), while ethylene/1-butene gives a symmetrical reaction leading to 1-butene and ethylene (Eq. 2, Scheme 2).



Scheme 2. The main metathesis reaction pathways

The high selectivity in propylene and 1-butene is also due to the metathesis reactions between the C6 oligomers and ethylene (Eq. 3-5). The contribution of the metathesis reaction between 1-butene and 2-butenes, leading to propylene and 2-pentene, can be also considered (Eq. 6).

In summary, we propose for the first time a catalytic method allowing the one-pot synthesis of both propylene and 1-butene from ethylene. This method is based on the use of two robust and highly active heterogeneous catalysts featuring large mesopores for a better transport of products, which are able to activate the reactions at 60 °C. No co-catalyst is required. The preliminary results reported here are very promising in terms of global selectivity to C3 and 1-C4 olefins (more than 86%) and yield (26 mmol_{C3} g_{catal}^{-1} h⁻¹ and 15 mmol_{1-C4} g_{catal}^{-1} h⁻¹ at the beginning of the process).

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: xxxxx Experimental details and results of the synthesis, characterization and behavior of the catalysts (PDF)

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Notes

The authors declare no competing financial interest.

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