

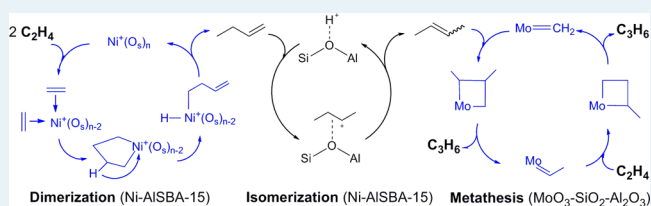
Ethylene to Propylene by One-Pot Catalytic Cascade Reactions

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Supporting Information

ABSTRACT: An original method for converting ethylene to propylene involving cascade oligomerization/isomerization/metathesis reactions over two robust and highly active heterogeneous catalysts is investigated. In a single flow reactor and under identical conditions, ethylene was first selectively dimerized/isomerized over Ni-*AlSBA-15* catalyst to form 2-butenes, which reacted then with the excess of ethylene over $\text{MoO}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ to produce propylene. At 80 °C and 3 MPa, specific activities up to 48 mmol of propylene per gram of catalyst per hour were obtained.

KEYWORDS: tandem catalysis, heterogeneous catalysis, oligomerization, metathesis, *Al-SBA-15*, nonhydrolytic sol-gel



Discovered in 1955, olefin metathesis has become one of the most important reactions for producing various chemicals in both petrochemistry and organic synthesis areas.^{1–4} In 1964, the first process involving metathesis (Triolefin process) was developed by Phillips Petroleum for converting propylene into highly demanded ethylene and 2-butene.⁵ Metathesis is a reversible reaction, and as the demand for polymer-grade propylene grew after the 1970s, metathesis was used in the Olefin Conversion Technology (OCT) licensed by ABB Lummus to produce propylene by conversion of an equimolar mixture of ethylene and butene over a supported W catalyst. Since then, a number of technologies based on OCT and W-, Re-, and Mo-based catalysts have been developed by other companies, such as BASF and Atofina, Mitsui Chemicals, BP Chemical, Sinopec Shanghai Petrochemical Processes.^{4,6}

A higher growth rate in the demand for propylene compared to ethylene 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 hydrocarbons. Ethylene is usually produced from crude oil derivatives (via steam thermal cracking), but alternative methods involving natural gas (via zeolite-catalyzed methanol-to-olefin process) or bioethanol conversion into ethylene, are very promising also. Several catalytic systems and strategies were proposed for the propylene production using only ethylene as a raw-material. Lyondell Petrochemical Co. developed in the 1980s a two-step process for the production of propylene, using the ethylene from ethane-cracking technology. First, using a homogeneous nickel catalyst, part of the ethylene is dimerized to 2-butene, which is reacted in a second step with the rest of the ethylene over a W/SiO₂ catalyst

to produce propylene.⁴ Pillai et al.⁷ reported the 2-step conversion of ethylene to propylene in a batch reactor by sequential use of homogeneous catalysts, $\text{Ni}(\text{acac})_2\text{-Et}_3\text{Al}_2\text{Cl}_3$ as a dimerization-isomerization catalyst, and $\text{WCl}_6\text{-Et}_3\text{Al}_2\text{Cl}_3$ as a metathesis catalyst.

Several works have been reported on the direct conversion of ethylene to propylene in a continuous, one-pot process, while avoiding the use of homogeneous catalysts. Thus, the direct conversion of ethylene to propylene over zeolites⁸ or SAPO⁹ catalysts at temperatures higher than 400 °C has been explored, but these catalysts showed a severe deactivation with time on stream. Iwamoto and co-workers¹⁰ and more recently Seidel-Morgenstern et al.^{11,12} and Hinrichsen et al.¹³ reported that nickel-loaded mesoporous materials catalyzed the conversion of ethylene to propylene, but only at temperatures higher than 350 °C. The catalytic tests were carried out at very low reactant feed rate (0.1–0.2 $\text{L}_{\text{C}_2\text{H}_4} \text{h}^{-1} \text{g}_{\text{catal}}^{-1}$) and the yield of propylene was about 30%. Basset and co-workers¹⁴ reported the direct transformation of ethylene to propylene over tungsten hydride supported on γ -alumina. At 150 °C and at a volume hourly space velocity of 260 h^{-1} , the selectivity to propylene was higher than 95%, but the ethylene conversion dropped rapidly from 40% to 10% over the first hours on stream.

Recently, Li et al.¹⁵ reported that a dual site bimetallic catalyst, $\text{NiSO}_4/\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$, prepared by coimpregnation, catalyzed the direct conversion of ethylene to propylene under mild reaction conditions (50 °C, 1 atm, GHSV of 2,682 h^{-1}). The two catalyst functions worked independently for

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dimerization (NiSO_4) and metathesis (Re_2O_7). However, the yield for propylene was lower than 30%, and the catalytic system rapidly deactivated.

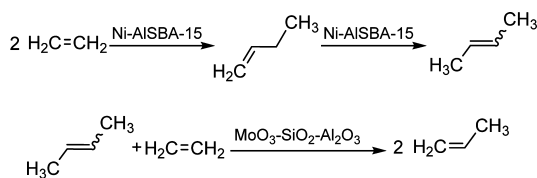
Rather than using a single, multifunctional catalyst, an option could be to use two (or more) distinct heterogeneous catalysts in a single reactor. This would offer increased control and allow using robust existing catalysts. However, there is no example of such a tandem catalysis coupling ethylene dimerization, butene isomerization, and metathesis to produce propylene, although several tandem reactions involving metathesis have been described.¹⁶

During the past decade, our institute has been working extensively for developing highly active and selective Ni^{2+} -based ordered mesoporous catalysts (Ni-*AlMCM*-41, Ni-*AlMCM*-48, and Ni-*AlSBA*-15) for the ethylene oligomerization.^{17–20} In particular, Ni-*AlSBA*-15 catalysts exhibited outstanding productivity and stability in the ethylene conversion to C4–C10 olefins (up to 175 g of oligomers per g of catalyst per hour at 150 °C and 3.5 MPa).²⁰ By choosing the reaction mode and parameters, the conversion of ethylene could be selectively directed to butenes or larger olefins.

In parallel, we have been developing in our institute an innovative nonhydrolytic sol–gel route²¹ for preparing mesoporous mixed oxides catalysts.²² The MoO_3 – SiO_2 – Al_2O_3 mixed oxides prepared by this route exhibited high specific surface areas, large disordered mesopores, and highly dispersed surface molybdenum species. They were found to be highly active and selective catalysts in the self-metathesis of propylene at low temperature.^{23,24}

In this context, the objective of this study was to investigate the conversion in a single flow reactor of ethylene to propylene under mild conditions, using two robust inorganic heterogeneous catalysts (Ni-*AlSBA*-15 and MoO_3 – SiO_2 – Al_2O_3) through tandem dimerization, isomerization, and metathesis reactions (Scheme 1). Note that both catalysts are stable in air and that no special precautions are needed for their storage and handling.

Scheme 1. Reaction Sequence: Ethylene Dimerization, Butene Isomerization, and Cross-Metathesis



The dimerization/isomerization catalyst, Ni-*AlSBA*-15, was prepared by grafting a *SBA*-15 silica support with sodium aluminate (NaAlO_2), followed by cation exchange, first with NH_4^+ then with Ni^{2+} . The exchanged sample was dried and then calcined for 5 h at 550 °C.²⁰ The metathesis catalyst, MoO_3 – SiO_2 – Al_2O_3 , was prepared by a one-step nonhydrolytic sol–gel method involving the reaction of chloride precursors (MoCl_5 , SiCl_4 , AlCl_3) with diisopropyl ether at 110 °C in an autoclave. The gel was dried by evaporation and calcined at 500 °C for 5 h.²³ The composition of the catalysts and their main textural characteristics are summarized in Table 1.

Ni-*AlSBA*-15 had a Si/Al ratio of 7.0 and a Ni content of 2.6 wt %. The corresponding Ni/Al ratio is 0.25, indicating an exchange level of NH_4^+ ions with Ni^{2+} of about 50%. As a consequence of this partial exchange level, Ni-*AlSBA*-15

Table 1. Composition and Texture of the Catalysts^a

catalyst	Si/Al mol/mol	Me wt %	D_p nm	V_p mL/g	S_{BET} m ² /g
Ni- <i>AlSBA</i> -15	7.0	2.6	7.6	0.75	450
MoO_3 – SiO_2 – Al_2O_3	14.4	6.5	8.1	1.12	540

^aMe = Ni or Mo, BJH average pore diameter (D_p), total pore volume (V_p), specific surface area (S_{BET})

contains Bronsted-type acidic sites, as *AlSBA*-15 materials.²⁰ MoO_3 – SiO_2 – Al_2O_3 had a Si/Al ratio of 14.4, and a Mo content of 6.5 wt % (0.75 Mo per nm²), corresponding to a MoO_3 loading of 9.7 wt %. Both catalysts were mesoporous (Figure 1), with high specific surface areas and large mesopores.

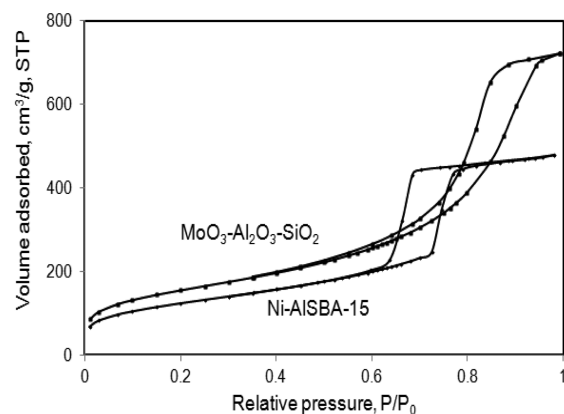


Figure 1. Nitrogen physisorption isotherms of Ni-*AlSBA*-15 and MoO_3 – SiO_2 – Al_2O_3 catalysts.

Large pore sizes are needed for ethylene oligomerization: microporous catalysts such as Ni-exchanged zeolites rapidly deactivate due to the blocking of micropores by heavy products.

The XRD pattern of Ni-*AlSBA*15 and of the starting *SBA*-15 material were similar (Figure S1), indicating that the long-range ordering of the pores was maintained after alumination and ion exchange.²⁰ On the other hand, Mo–Si–Al was amorphous to XRD, confirming the absence of crystalline MoO_3 , whereas the sorption isotherm ruled out any long-range ordering of the mesoporosity.²⁴

In a recent study,²⁰ we showed that Ni-*AlSBA*-15 was a highly active and stable catalyst for the ethylene oligomerization carried out in flow mode, under various conditions: $T = 50$ – 150 °C, $p = 1.0$ – 4.0 MPa, and mass hourly space velocity (WHSV) = 10 – 17.5 h^{–1}. Butenes, hexenes, and octenes were the major products. The reaction conditions had a decisive influence on the ethylene conversion and the oligomer distribution. The increase of temperature, residence time, and pressure resulted in an increase of the ethylene conversion, a decrease of the selectivity to butenes, and an increase of the double bond isomerization within the butene fraction. MoO_3 – SiO_2 – Al_2O_3 mixed oxides were found highly active in the metathesis of propene²⁵ as well as in the metathesis of ethylene and butene²³ at 40 °C, with specific activities of about 45 mmol g^{–1} h^{–1} for a catalyst with a Si/Al ratio of ≈ 14 and a Mo loading of 12.5 wt %.

In order to produce propylene from ethylene (according to Scheme 1), two consecutive catalyst beds consisting of Ni-*AlSBA*-15 and MoO_3 – SiO_2 – Al_2O_3 , respectively, were placed in the reactor. On the basis of previous results obtained in the oligomerization and metathesis reactions and preliminary

experiments, the following parameters were chosen for conducting the oligomerization–metathesis reactions: $T = 80\text{ }^{\circ}\text{C}$, $p = 3.0\text{ MPa}$ and flow rate = 33 mL min^{-1} of pure ethylene. WHSV was 16.5 h^{-1} for the oligomerization catalyst (0.15 g) and 5 h^{-1} for the metathesis catalyst (0.50 g). A moderate conversion of ethylene is favorable, because it limits the formation of higher oligomers in the oligomerization step and increases the conversion in the metathesis step.

Figure 2 shows typical chromatograms obtained with one catalyst (Ni-ALSBA-15) and two catalysts (Ni-ALSBA-15 and

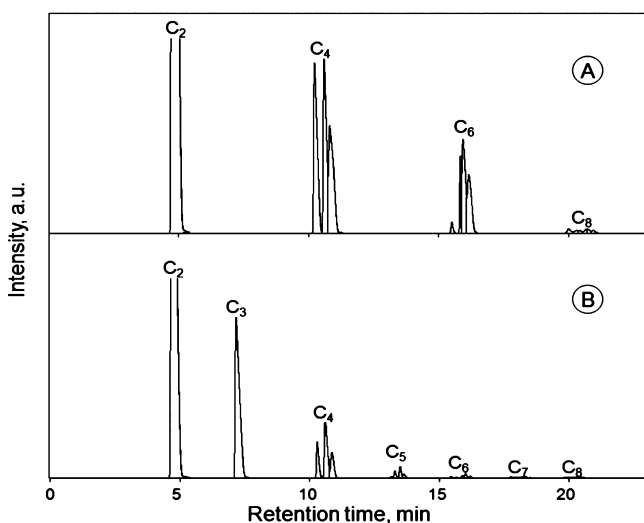


Figure 2. Typical chromatograms for ethylene oligomerization over Ni-ALSBA-15 (A) and oligomerization–metathesis over Ni-ALSBA-15 + $\text{MoO}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ (B); Conditions: $80\text{ }^{\circ}\text{C}$, 3.0 MPa of ethylene.

$\text{MoO}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$). Over Ni-ALSBA-15, butenes were the major products, but small amount of C6 and C8 olefins were also formed. In the C4 fraction, the only detected molecules were the three *n*-butene isomers: 1-C4, *trans*- and *cis*-2-C4. Both ethylene conversion ($28 \pm 1\%$) and oligomer distribution did not change during 6 h on stream. In the presence of the two catalysts, besides C4, C6, and C8 olefins, propylene, pentenes, and heptenes were also formed.

Under the present reaction conditions, the major olefins were propylene and butenes (>90%). The selectivity to C5, C6, and C7+ olefins was 4–5%, 3–4%, and 1–2%, respectively. The presence of C5 and C7 olefins indicate that $\text{MoO}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ was also able to catalyze metathesis reactions involving olefins higher than C4.

The selectivity profiles to C3 and C4 as a function of time on stream are given in Figure 3. The initial selectivity to propylene reached 70% but decreased progressively to 46% at 5 h on stream. The selectivity to butenes increased from 22% to 48%. Note that the conversion of ethylene was quasi-constant at $40 \pm 2\%$ throughout the reaction period. These results indicate that the activity of the metathesis catalyst diminished with time on stream, whereas the oligomerization catalyst maintained its activity during the catalytic test. Deactivation is a rather systematic drawback for metathesis catalysts, due mostly to the poisoning of the active centers by strongly adsorbed reaction products. In our system the low reaction temperature may contribute to the deactivation process by preventing fast product desorption. Further studies will be needed to determine optimal conditions allowing to avoid, or at least minimize, such a limitation.

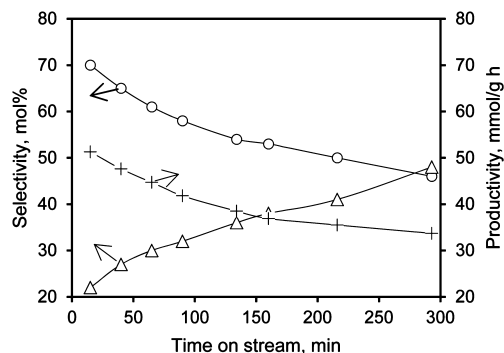


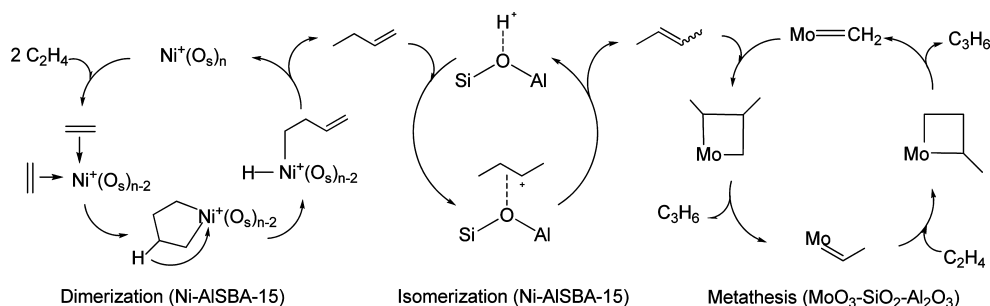
Figure 3. Selectivity to propylene (o), butenes (Δ) and productivity in propylene (+) vs time on stream. Conditions: $80\text{ }^{\circ}\text{C}$, 3.0 MPa of ethylene.

The specific activity of the catalysts for the C3 formation (in $\text{mmol}_{\text{C}_3}\text{ g}_{\text{catal}}^{-1}\text{ h}^{-1}$) was also reported in Figure 3. Although it decreased from 51.3 to $33.7\text{ mmol g}^{-1}\text{ h}^{-1}$ with the time on stream, these values are remarkably high. Indeed, they are close to the values reported for Mo–Si–Al nonhydrolytic sol–gel catalysts with similar compositions, previously used for the self-metathesis of propylene to ethylene and butenes²⁵ or in the metathesis of ethylene and *trans*-2 butene to propylene.²³ Considering the total number of Mo atoms in the catalyst, a specific activity of $51.3\text{ mmol}_{\text{C}_3}\text{ g}_{\text{catal}}^{-1}\text{ h}^{-1}$ corresponds to $277\text{ mmol}_{\text{C}_3}\text{ mmol}_{\text{Mo}}^{-1}\text{ h}^{-1}$ ($4.6\text{ mol}_{\text{C}_3}\text{ mol}_{\text{Mo}}^{-1}\text{ min}^{-1}$).

The mechanism of the ethylene oligomerization using metal-based homogeneous catalysts involves the insertion of ethylene into an initial metal–alkyl^{26,27} or a metal–hydrogen bond.²⁸ A cocatalyst is required for generating the metal-active species. Such a growth mechanism seems unlikely for the oligomerization of ethylene catalyzed by nickel ions dispersed on inorganic supports because neither metal–alkyl nor metal hydride species are initially formed on these materials in the absence of a cocatalyst.

In two interesting studies published in the 80s,^{29,30} it has been shown that it was possible to produce supported Ni^+ ions on zeolites and SiO_2 . These dispersed Ni^+ ions can reversibly bind ligands (L) such as C_2H_4 , C_3H_6 , or surface oxide ions O^{2-} leading to various $\text{Ni}(\text{L})_n^+$ species. The oligomerization mechanism involves a metallacyclopentane intermediate resulting from a concerted coupling of two olefin molecules on each Ni^+ center. Such a mechanism has also been suggested for the ethylene dimerization over phosphine–Ni complexes.³¹ In a previous study³² we showed that during the treatment at temperatures higher than $500\text{ }^{\circ}\text{C}$ under a dry atmosphere, the initial Ni^{2+} ions in Ni-MCM-41 and Ni-Y catalysts were dehydrated and reduced to Ni^+ ions. On the basis of these data, we propose for the ethylene dimerization step the mechanism shown in Scheme 2, where two molecules of coordinated ethylene at a nickel ion react by oxidative coupling to form a metallacyclopentane intermediate, which then forms 1-butene by β -hydride transfer.³³

When the desorbed 1-butene migrates to an acid site, it is easily converted to internal double-bond olefin, as shown in a simplified manner in Scheme 2. Note that double-bond shift in alkenes is an extremely facile reaction, exhibiting turnover frequencies up to 10^7 s^{-1} in heterogeneous acid catalysis.³⁴ Hartmann et al.³⁵ showed that the isomerization of 1-butene to *cis*-2-butene and *trans*-2-butene can be efficiently catalyzed by Al-MCM-41 materials.

Scheme 2. Proposed Mechanism for the Conversion of Ethylene to Propylene ($O_s = O^{2-}$ Surface Oxide Ions)

The cross-metathesis of ethylene and 2-butenes over the $MoO_3-SiO_2-Al_2O_3$ catalyst most likely involves the initial formation of carbene species ($Mo=CHR$, $R = H$ or alkyl),⁶ followed by the formation of metallacyclobutane intermediates, as proposed in Chauvin's reaction mechanism.^{36,37}

In summary, we have proposed an original cascade catalytic method allowing the one-pot continuous synthesis of propylene from ethylene. This method is based on the use of two robust and highly active heterogeneous catalysts developed in our institute. The preliminary results reported here are promising in terms of catalyst productivity and selectivity to C3–C4 olefins, but additional work is needed to optimize conditions in order to improve catalyst lifetime and selectivity to propylene.

■ ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00383.

Experimental details of the synthesis and characterization of the catalysts (PDF)

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Notes

The authors declare no competing financial interest.

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