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Propylene Synthesis via Isomerization-Metathesis of 1-Hexene and FCC olefins

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Conversion of 1-hexene or olefins obtained by fluid catalytic cracking (FCC) to propylene via isomerization-metathesis (ISOMET) were investigated using ethylene, as cross-coupling agent. Zeolite H-beta (HBEA) was applied as isomerization catalyst. The olefin metathesis (OM) catalysts were about 12 wt% molybdena, supported on zeolite beta (MoO3/HBEA), and y-alumina (MoO3/Al2O3). HBEA supported catalyst with a lower molybdena content (6 wt%) was also investigated. The catalysts were characterized by X-ray diffractometry (XRD), H2-temperature-programmed reduction (H2-TPR), Fourier Transform Infrared (FT-IR), visible Raman, in-situ Ultraviolet-Visible (UV/VIS) and XPS spectroscopies. It was shown that HBEA is highly active and robust catalyst of double bond isomerization. Applying a physical mixture of HBEA and 12MoO3/Al2O3 catalyst at 150 °C and 3 bar ethylene pressure 60 % conversion of 1-hexene to propylene was attained. Interestingly, quantitative conversion to propylene was achieved after reactivation of the deactivated catalyst in argon atmosphere at 550 °C. It has been found that the pre-treatment of the catalyst with olefins such as ethylene before inert gas activation resulted in significant catalyst activity improvement. This suggests that the adsorbed olefins may play key role in the formation of active metal centers during the catalyst reactivation process. The catalyst mixture had also good performance in the conversion of FCC olefins to propylene. The MoO3/HBEA catalysts have rendered reasonable activity, however, the catalyst showed significantly shorter lifetime than the alumina-containing catalyst mixture.

Introduction

Olefin metathesis (OM) is a powerful and versatile method of organic chemistry. During OM carbon atoms of two C=C double bonds are reorganized to new double-bond-containing molecules. These reactions are very selective and require mild reaction conditions. The atom economy of the synthetic procedures is often 100%, i.e., all the starting materials are incorporated into the products.

Nature is abundant in bio-based materials, containing olefin bond. Low value olefins can also be found in vast amounts in petrochemical by-products. These chemicals often appear as an underutilized feedstock.

With the advent of alternative fuels and electric cars, the worldwide demand for mineral oil-based fossil fuels will certainly decrease. However, the need for high value innovative materials, including advanced polymers steadily increases.3-5 Unfortunately, at present, these demands cannot be met by using renewable feedstocks only. Therefore, there is still a constant need for the development of high atom economic chemical procedures for the efficient and environmental benign conversion of petrochemicals to high value materials.

Propylene is an emerging bulk chemical, the key monomer of polypropylene plastic and other commodity chemicals. It is mainly obtained as by-product of ethylene production in steam cracker units.6,5 Possibilities to control the ratio of ethylene to propylene in the cracked product mixture are limited. As a result, cracking units are currently producing excess ethylene, while the increasing demand for propylene remains uncovered.6-9 Propylene can also be synthesized on large scale by propane dehydrogenation, as well as Fisher-Tropsch synthesis, and methanol to olefin conversion,10-12 Propylene can be produced selectively also via OM under moderate reaction conditions. The most general example is the ethenolysis of 2-butene giving two propylene molecules.1,4,5,7,9,11-14

There are several industrial examples for OM of olefinic hydrocarbon over heterogeneous catalyst. Such as the Shell higher olefin process (SHOP) for detergent production,15 the Philips Triolefin Process for synthesis of 2-butenes16 and the Olefin Conversion technology used by ABB Lummus Global for propylene production.17 The most widely used catalyst systems includes Mo11,14,18-22 W1,4,6,8,9,12,18,23-25 or Re2,26,27 oxides. Mo and W-based catalysts are widely used in the petrochemical industry. Some new OM reactions, catalysed by metal-oxide, have been reviewed recently.10,28

A special case of OM is the isomerization-metathesis (ISOMET). During ISOMET, the olefinic bonds migrate along the hydrocarbon chain (isomerization), which is followed by a cross-metathesis reaction with another olefin, a cross-coupling agent. The special case of OM, when the cross-coupling agent is ethylene is called ethenolysis.10,29 In case of linear mono-olefins, the complete ISOMET using ethylene as cross-coupling agent theoretically ends up in propylene as the only end product (Scheme 1).

The ISOMET of C4 and C5 olefins producing propylene is one of the most widely investigated area. Interestingly, industrially applied systems are mainly based on W (5-10% on silica) or Re (5-10 % on alumina) catalyst systems.6,11,30-32 The ISOMET process of higher olefins (C4-C9) and the mixtures thereof, has also been patented.33 Re2O7, WO3 and MoO3 were used as OM catalysts, whereas RuO2, MgO and K2CO3 were applied as isomerization catalysts. Another patent application describes a process for converting an olefin feed containing butenes,
diolefins and polyolefins to propylene with ethylene using molybdenum as metathesis catalyst and MgO, K$_2$CO$_3$, K$_2$O as isomerisation catalyst. In both cases, the use of FCC mixture (fluid catalytic cracking) is mentioned as a source of olefin feed, but only after appropriate refining. The FCC and FCC light fractions are abundant in C$>$5 olefins. For example, the ethenolysis of oleic acid produces 1-decene, while the ethenolysis of linoleic acid gives 1-hexene. Both vegetable oils are highly abundant in the nature. Light olefins (propylene, butenes, butadiene) are also available from biomass originated bioethanol and biobutanol and from biomass pyrolysis. Both micro- and mesoporous silicates, aluminosilicates were shown to be effective as supports for biomass pyrolysis. Not only petrochemical streams but components. Furthermore, not only petrochemical streams but also materials derived from renewable feedstocks may contain C$>$5 olefins. The monolayer coverage of the used molybdena is about two-third of the monolayer capacity. The absence of the MoO$_3$ crystallites are well dispersed on the alumina surface, thus they correspond to about 19.2 wt% MoO$_3$ content. The absence of the MoO$_3$ XRD reflections suggests that MoO$_3$ crystallites are well dispersed on the alumina surface. Papers reporting isomerization metathesis using C$>$5 alkenes as raw materials for propylene synthesis are rare. Especially there is no information in the literature about the synthesis of propylene from C$>$5 alkenes via ISOMET using HBEA as isomerization and MoO$_3$/Al$_2$O$_3$ as olefin metathesis catalysts. This paper describes a zeolite-supported molybdena (MoO$_3$/HBEA) catalyst systems having isomerization (HBEA), as well as metathesis (MoO$_3$) activity. The mixed bed of alumina-supported molybdena and zeolite beta (MoO$_3$/Al$_2$O$_3$/HBEA) ISOMET catalyst is also reported. MoO$_3$ loading of about 12 wt% was applied on both supports. Based on the work of Li and co-workers, for HBEA, a catalyst containing lower MoO$_3$ loading (6 wt%) was also investigated. The catalysts were characterized and investigated in ISOMET of 1-hexene model compound with ethylene. Conversion of FCC having high olefin content to propylene was also studied. It has been found that the initial catalytic activity can be significantly improved by simple high temperature heat treatment of the deactivated ISOMET catalyst in an inert gas.

**Results and discussion**

The molybdena content of the catalysts, determined by ICP-OES, is shown in Table 1. The ISOMET activity of 13MoO$_3$/HBEA and the physical mixture of 12MoO$_3$/Al$_2$O$_3$ and HBEA were higher than that of 6MoO$_3$/HBEA (vide infra). The effect of the amount of MoO$_3$ loading on HBEA zeolite (70%)/Al$_2$O$_3$ (30%) has been investigated by Li et al. Using the above-mentioned solid support mixture, a 6-8% molybdena loading was found to be optimal. The characterization of 13MoO$_3$/HBEA and 12MoO$_3$/Al$_2$O$_3$ is presented below, whereas the properties of 6MoO$_3$/HBEA are included in the ESI.

**Catalyst characterization**

**Structure and texture** The XRD patterns of Al$_2$O$_3$, HBEA supports, and 12MoO$_3$/Al$_2$O$_3$, 13MoO$_3$/HBEA catalysts are shown in Fig. 1. Gamma-alumina is the only detectable phase of the above-mentioned solid support mixture. A 6-8% molybdena loading was found to be optimal. The characterization of 13MoO$_3$/HBEA and 12MoO$_3$/Al$_2$O$_3$ is presented below, whereas the properties of 6MoO$_3$/HBEA are included in the ESI.

**Table 1** Characterization of the supports and catalysts

| Catalyst     | MoO$_3$ wt% | SSA $^a$ | H$_2$ uptake $^b$ | H/Mo $^c$ |
|--------------|-------------|----------|-------------------|-----------|
| Al$_2$O$_3$  | -           | 192      | -                 | -         |
| 12MoO$_3$/Al$_2$O$_3$ | 11.7 | 184 | 2.38 | 5.9 |
| HBEA (Si/Al =12) | - | 480 | - | - |
| 13MoO$_3$/HBEA | 13.5 | 235 | 2.61 | 5.6 |
| 6MoO$_3$/HBEA | 6.1 | 476 | 1.17 | 5.6 |

$^a$determined by ICP-OES, $^b$Specific Surface Area (SSA) determined by the Brunauer-Emmett-Teller method, $^c$calculated from the TPR curve measured up to 800 °C.
In addition, intense reflections typical of orthorhombic MoO$_3$ (JCPDS 35-609) appeared in the XRD pattern of 13MoO$_3$/HBEA at $2\theta = 27.4^\circ$, 23.4$^\circ$ and 25.7$^\circ$. The average MoO$_3$ particle size, calculated from the Scherrer equation using the $2\theta = 27.4^\circ$ reflection, was about 90 nm. At lower MoO$_3$ loading (6MoO$_3$/HBEA) no crystalline MoO$_3$ phase was detected by XRD and the diffraction lines of the zeolite support was more intense (Fig. S1). No crystalline Al$_2$(MoO$_4$)$_3$ phase was detected in these samples. Formation of this phase was found in samples treated at high-temperature (680 °C). In our case, however, the MoO$_3$ content was not high and the decomposition temperature of the Mo precursor was lower, 500 °C, so the formation of the aluminium molybdate phase is unlikely in any of the supports. As expected, the specific surface area of the molybdena-loaded catalyst was smaller than those of the corresponding support. The difference in the surface areas depends on the pore size of the support (Table 1). For γ-Al$_2$O$_3$, which is mesoporous, the specific surface area decreased only slightly, (from 192 to 184 m$^2$/g). The specific surface area of the microporous zeolite catalyst with 12 wt% MoO$_3$ loading, however, was only half of that of the zeolite support (235 and 480 m$^2$/g). At 6 wt% of MoO$_3$ content the SSA of HBEA did not decrease (476 m$^2$/g).

Temperature-programmed reduction by hydrogen (H$_2$-TPR)

Reducibility of the molybdenum species in 12MoO$_3$/Al$_2$O$_3$ and 13MoO$_3$/HBEA was investigated by temperature-programmed H$_2$ reduction (Fig. 2). Two reduction peaks were observed on the H$_2$-TPR curve of the 12MoO$_3$/Al$_2$O$_3$ catalyst. The low-temperature peak in the range of 300-600 °C with a maximum of 450 °C represents the reduction of multilayered and octahedral Mo(VI) to Mo(V). The tetrahedral Mo (IV) species has stronger interaction with the Al$_2$O$_3$ support leading to a reduction temperature in the range of 600-800 °C. In this higher temperature region the reduction of Mo(IV) to Mo(0) takes place.

For the 13MoO$_3$/HBEA catalyst, two reduction peaks were observed in the temperature range of 300-650 °C and 650-800 °C. The peak at lower temperature is assigned to reduction of Mo(VI) to Mo(IV) as in case of the 12MoO$_3$/Al$_2$O$_3$ catalyst. The second peak represents the complete reduction of Mo(IV) to Mo(0). Similar TPR curve was observed for 6MoO$_3$/HBEA (Fig. S2). Table 2 shows that the hydrogen uptake, expressed in H/Mo ratio, in the Al$_2$O$_3$-supported sample was 5.9. This amount of hydrogen consumption is near to the amount needed to the total reduction of MoO$_3$ to Mo(0) (6). Molybdena has been shown to react with the zeolitic protons during oxidative decomposition of the heptamolybdate precursor. At 500 °C, MoO$_3$ oligomers migrate into the channels and react with the Brønsted acid sites of the zeolite to form ditetrahedral Mo species, i.e. (Mo$_2$O$_7$)$^{2+}$ cations. These cationic Mo species can only be reduced at temperatures above 800 °C. Table 1 shows that H/Mo ratio was 5.6 for both MoO$_3$/HBEA catalysts, suggesting that some Mo may occupy cationic positions and cannot be reduced under our TPR conditions. In line with the above results, the loss of Brønsted acid sites was also observed for these samples (vide infra).

Before catalytic experiments, the calcined catalysts were activated in-situ in a flow of Ar at 550 °C. Thermal autoreduction of Mo(VI) cannot be detected by H$_2$-TPR.

**FT-IR spectroscopy of adsorbed pyridine**

For the ISOMET reaction, the catalyst must contain Brønsted-acid sites that promote double-bond isomerization of terminal olefins. Pyridine adsorption, followed by FT-IR spectroscopy, was used to characterize the acidity of the supported molybdena catalyst (Fig. 3). Brønsted and Lewis acid sites of the catalysts can be distinguished by the characteristic 19b/8a ring vibrations of pyridinium ions and pyridine bound to Lewis acid sites.
These vibrations of the two species appear in different regions of the spectrum, i.e., at 1545/1637 cm\(^{-1}\), and around 1455/1620 cm\(^{-1}\), respectively. Fig. 3 shows that the HBEA support has both Brønsted and Lewis acid sites. In zeolites, Brønsted acidity is due to protons compensating negative charge on the zeolite framework generated by tetrahedral framework aluminum. Extra-framework aluminum represents Lewis acid sites. High amount of defect sites caused by crystallographic faults is typical for the structure of zeolite Beta.\(^{27}\) So, trigonal framework aluminum near the silanol nests shows Lewis acidity. Upon Mo-loading, the number of both Brønsted and Lewis acid sites decreased significantly. The FT-IR results suggest that molybdenum reacts with zeolitic protons and occupies cationic positions as ditetrahedral Mo ions (Mo\(\text{O}_2\))^\(^{2+}\) suggested by Ding et al.\(^{58}\) The amount of Brønsted acid sites in the zeolite sample was 0.71 mmol g\(^{-1}\), measured by the ammonium ion exchange capacity. Comparing the band intensities of the pyridinium ions around 1545 cm\(^{-1}\) the number of Brønsted acid sites decreased by 36 %, indicating that 0.12 mmol g\(^{-1}\) Mo is in the cationic position, which is about 15% of the total Mo content. In addition, surface Mo\(\text{O}_x\) species can be bound in the zeolite silanol nests both in the micropores and on the outer surface of the zeolite crystallites. These species cause a significant decrease in the number of Lewis acid sites.

In the spectrum of 12MoO\(_3\)/Al\(_2\)O\(_3\) the intensities of the bands characteristic of Lewis acid sites slightly increase at 1453 and 1621 cm\(^{-1}\) compared to the bare support (Fig. 3). Highly polymerized Mo\(\text{O}_x\) species were suggested to be responsible for the additional Lewis acid sites at this Mo content.\(^{59}\) App. a 10 % decrease in Brønsted sites was observed on 6MoO\(_3\)/HBEA relative to the HBEA support (Fig. S3).

Raman spectroscopy

The structure of supported molybdenum oxide was investigated by Raman spectroscopy under ambient conditions, in hydrated state. The Raman spectra of 12MoO\(_3\)/Al\(_2\)O\(_3\) and 13MoO\(_3\)/HBEA are presented in Fig. 4. In the spectrum of 12MoO\(_3\)/Al\(_2\)O\(_3\), the bands observed at 953, 910 and 355 cm\(^{-1}\) are assigned to the symmetric stretching, asymmetric stretching, and bending vibrations of the terminal Mo=O bond of octahedral Mo\(\text{O}_6\) species in hydrated heptamolybdate, respectively.\(^{60}\) In addition, the bands at 566 and 222 cm\(^{-1}\) are due to the Mo-O-Mo symmetric stretching and deformation vibrations of these molybdena species, respectively. These results confirm that 12 wt% of molybdena loading octahedral species dominate on alumina. It should be mentioned that tetrahedral Mo\(\text{O}_x\) units is also present as the Raman band at 910 cm\(^{-1}\) is typical of the symmetrical stretching vibrations of the terminal Mo=O in tetrahedral molybdena species.\(^{61}\) This observation was also confirmed by UV-VIS spectroscopy. The intense and narrow bands in the spectrum of 13MoO\(_3\)/HBEA is due to crystalline Mo\(\text{O}_3\),\(^{62}\) indicating that this catalyst contains Mo\(\text{O}_3\) phase, which is also supported by the XRD data (Fig. 1). At 6 wt% molybdena loading, the intensity of the 970 cm\(^{-1}\)-band increased, compared to the zeolite support (Fig. S4). This indicates that the catalyst contains tetrahedral Mo\(\text{O}_x\) species.

\textit{In-situ} UV-VIS spectroscopy

\textit{In-situ} UV-VIS experiments were performed to determine the type of Mo\(\text{O}_x\) species in the calcined 12MoO\(_3\)/Al\(_2\)O\(_3\) and 13MoO\(_3\)/HBEA catalysts, and to follow changes of the polymerization degree of Mo\(\text{O}_x\) during \textit{in-situ} activation in an inert atmosphere (Ar) at temperatures increased up to 550 °C (Fig. 5). Both calcined catalysts show a strong absorption band below 330 nm. The bands at 250 and around 290 nm are due to the ligand–metal charge transfers (LMCT) from oxygen to Mo(VI) in highly dispersed and small linear-chained tetrahedral
MoO₃ respectively. LMCT in polymerized octahedral MoO₃ give rise a band around 330 nm. For 12MoO₃/Al₂O₃, the intensity of the absorption band at 250 nm becomes weaker above 200 °C, while the band at 330 nm gains strength. This result suggests that during thermal treatment in inert atmosphere tetrahedral MoO₃ is transformed to polymerized octahedral MoO₃ species on alumina-supported molybdena. Comparing the relative intensity of the bands below 300 nm and above 200 °C, similar but smaller changes were observed, indicating that a smaller portion of tetrahedral MoO₃ species is transformed to octahedral MoO₃ species on the zeolite-supported molybdena. MoO₃ located in microporous channels is less capable to form longer MoO₃ chains. They can be formed only on the outer surface of the zeolite crystals, but in small amounts only because the outer surface is only approx. 4-5% of the specific surface area of the zeolite crystals. 

XPS measurements

Quantitative evaluation of the XPS data indicated that the Mo-oxide content of the MoO₂/Al₂O₃ catalyst was around 12 wt%, in good agreement with the nominal composition. Spectral features of Al (Al 2p binding energy of 74.7 eV, Al KLL kinetic energy of 1386.8 eV and the Auger parameter defined as their sum at 1461.5 eV) as well as the main O 1s peak around 531.4 eV all pointed to an oxidized/hydroxylated environment for the Al(III) cations, in agreement with literature data on similar catalysts. No significant changes in the chemical environment of Al were observed during the treatments. In addition, no sign of dissolution of Mo into the alumina was detected. The Mo 3d₅/₂₋₃/₂ spin orbit doublet of well-dispersed MoO₃ on alumina has a rather broad line shape with a 3d₅/₂ binding energy around 233 eV which is somewhat higher than the value characteristic for bulk MoO₃ (232.5 eV). While the shift is attributed to the strong interaction of the oxidized Mo species with the alumina support, the broadening can be the result of a charging effect, but may also indicate the existence of a range of slightly different environments for the adsorbed Mo(VI) ions. As it is shown in Fig. 6a, these features are well reproduced in the Mo 3d spectrum of the calcined 12MoO₃/Al₂O₃ sample exposed to air. The spectrum can be well modelled by a single peak pair with the 3d₅/₂ component at 233.2 eV, indicating the exclusive presence of Mo(VI) ions. Treatment in Ar at 550 °C resulted in a marginal shift of the maximum of the spectrum towards lower binding energies and further apparent broadening (Fig. 6b). Spectral modelling revealed that these changes can be interpreted as the result of the appearance of a new Mo 3d doublet with its 3d₅/₂ peak around 231.7-231.9 eV. According to its binding energy, this new component was attributed to Mo(V) species. The abundance of the Mo(V) species clearly increased upon ethylene exposure (Fig. 6c) and some further increase was observed after the subsequent treatment in Ar at 550 °C (Fig. 6d). Although the combination of the Mo(VI) and Mo(V) states adequately modeled the observed line shapes, the broad peaks can easily shadow weak Mo(IV) contributions, so their presence – especially after the ethylene exposure and the subsequent re-activation – cannot be completely ruled out.

Fig. 5 In-situ UV-VIS spectra of the 12MoO₃/Al₂O₃ and 13MoO₃/HBEA catalysts. The catalysts were heated at a rate of 10 °C/min up to 550 °C for 2 h in Ar flow.

Fig. 6 Mo 3d spectra of the calcined 12MoO₃/Al₂O₃ sample exposed to air (a), after activation in Ar at 550 °C for 1 h (b), subsequent C₂H₄ exposure at 100 °C for 1 h (c) and after reactivation in Ar at 550 °C for 1 h.
1-Hexene isomerization over HBEA catalyst

Preliminary experiments have been carried out to investigate the isomerization of 1-hexene model compound using HBEA catalyst at 75 °C and atmospheric pressure in inert Ar gas atmosphere. At nearly 90 % 1-hexene conversion, the yields of cis- and trans-2-hexane and cis- and trans-3-hexene were 70 and 20 %, respectively. (Fig. 7). This result indicates that double bond shift and cis-trans rearrangement are the main reactions in the conversion of 1-hexene over zeolite beta, consistent with earlier results on large- and medium-pore zeolites, i.e., H-Y and H-ZSM-5. Side reactions, such as polymerization are negligible. It was demonstrated that under these conditions, HBEA is highly robust. No catalyst deactivation was observed during a time on stream (TOS) of 10 h.

The ISOMET of 1-hexene with ethylene was performed at 3 bar total pressure of and at ethylene/1-hexene molar ratio of 10. In order to make sure that the isomerization is not affected by ISOMET condition the isomerization reaction was performed in the presence of 3 bar of ethylene (optimal ethylene pressure for OM, Fig. S7), as well. The results showed that neither the catalytic activity nor the product selectivity was affected. Similar conversion and reaction product distribution was observed as in the absence of ethylene. The influence of reaction temperature on the isomerization conversion and product distribution has been investigated at 75 (optimal reaction temperature for OM), 100, 125 and 150 °C and 3 g cat B1-μmol h space time under 3 bar ethylene pressure. It could be concluded that even at 75 °C neither the conversion of 1-hexene nor the product distribution have been changed significantly.

By using the optimized OM (ethenolysis) condition, the catalyst activity did not decrease within ten hours of the reaction (Fig. 7). The yield of 2-hexenes achieved 66 % (55 % trans-2-hexene and 11 % cis-2-hexene) after 1 hour TOS. HBEA is a highly robust isomerization catalyst showing high activity and stability at optimized metathesis reaction conditions.

The 1-hexene isomerization activity of the MoO3-containing HBEA catalysts was also investigated. The catalysts were pretreated in O2 flow at 550 °C for 2 h, to keep Mo in Mo(VI) state. It was found that the isomerization activity of HBEA significantly drops upon impregnating with MoO3. With increasing MoO3 content, the number of Brønsted acid sites decreases (shown by FT-IR spectroscopy) therefore the isomerization activity also decreases. Actually, at 6 wt% loading 80 % 1-hexene isomerization was observed (versus 90 % on neat HBEA), meanwhile at 12 wt% loading the isomerization activity was around 60 % after one hour of time on stream. At 12 wt% molybdena content the isomerization activity was halved after 5 hours of time on stream, whereas 6MoO3/HBEA shows good stability in 1-hexene isomerization.

1-Hexene ISOMET using MoO3/HBEA catalysts

Theoretically, terminal olefins (not only) such as 1-hexene can be completely converted to propylene by using ethylene in sequential isomerization and ethenolysis steps (ISOMET) (Scheme 2). Two types of sites are required, Brønsted sites for the C=C double-bond isomerization of 1-hexene and the intermediate alpha-olefins formed (1-pentene, 1-butene), and active MoO3 sites for the conversion of isomerized olefins (2-, 3-hexenes, 2-pentenes, 2-butenes) with ethylene to give propylene and lower alpha-olefins (1-pentene, 1-butene). The pathway of 3-hexene isomer to propylene is shorter, as its reaction with ethylene gives 1-butene, which is converted to propylene in the isomerization and ethenolysis steps (not shown in Scheme 2).

In the following series of experiments, HBEA was used not only as an isomerization catalyst but also as a support for MoO3. The reactions have been carried out under 3 bar ethylene pressure and 3 g cat B1-μmol h space time in the temperature range of 75-150°C. The catalyst was pre-treated in inert gas at 550 °C and the activated catalyst thus obtained was tested in ISOMET reaction for 3 h of time-on-stream (TOS). After activation, the catalyst was regenerated under the same conditions as the pretreatment. The activity of the reactivated catalyst was also studied in ISOMET reaction.

Fig. 7 Isomerization of 30 % 1-hexene (1-H) solution using HBEA catalyst at 75 °C and 3 g cat B1-μmol h space time under 3 bar ethylene pressure. The calcined catalyst was pretreated in-site in a flow of Ar (50 ml/min) at 450 °C for 2 h, at atmospheric pressure.

Scheme 2 Subsequent isomerization and ethenolysis steps in ISOMET of 1-hexene with ethylene to propylene. (The pathway of the 3-hexene isomer is not shown here.)
On the activated 13MoO3/HBEA catalyst, the propylene yield was low, ranging from 10 to 29 % at 0.5 h of TOS (Table 2). It was 10 % at 75 °C, with increasing reaction temperature reached its maximum (29 %) at 125 °C and then at 150 °C decreased to 19 %. Reactivation, i.e., heat treatment in an inert atmosphere at high temperature (550 °C) after the ISOMET reaction, however, resulted in a significantly increase in the initial activity of the 13MoO3/HBEA catalyst. At 75 °C, the propylene yield doubled, while at higher temperatures the propylene yield dropped significantly, from 85 to 10 %.

At 75 °C the activity of the two catalysts were about the same, but as the temperature increased, the propylene yield on 6MoO3/HBEA hardly changed. The number of active sites is presumably decreasing during the reaction as carbonaceous deposits may gradually block the micropores, thus the reactants molecules cannot access the active sites located inside the pores. Not only coking, but also the low oxidation state of Mo is also a reason of the decreased activity (vide infra).

To reactivate catalysts the Brønsted acid sites of HBEA zeolite support protonate the 2-hexene to form the carbenium ion intermediate of double bound isomerization.77-79 Zhang et al.11 reported that both the number of Brønsted acid sites and the high dispersion of MoO3 species has an important role in determining the OM activity.

Brønsted acid sites not only catalyse double-bond isomerization of alpha-olefins, but are also involved in the OM reactions, i.e., participate in the generation of active metal carbene species, which are the active site of the OM reactions. Previous work suggested that Brønsted acid OH groups interact with adjacent metal oxides, for example, MoOx, WOx, or ReOx for the generation of OM active carbene species.80,81 Recent results showed that using MoO3/SBA-15 catalyst, surface Brønsted acidic OHs coordinated to Mo(VI) protonate propylene and isopropoxide species are formed upon propylene adsorption.82 Such species are further oxidized by lattice oxygen of MoOx, to gas-phase acetone yielding reduced Mo(IV). This species reacts with gas-phase propylene to form the OM active Mo(VI)-alkylidene species. When Brønsted acid sites and MoOx species were located on the microporous support, rapid deactivation occurred during the ISOMET reaction.

The complementary characterization techniques revealed that in the 13MoO3/HBEA sample Mo exists in highly dispersed tetrahedral and polymerized octahedral MoOx species, which are active in the OM reaction. However, a fraction of Mo is present as catalytically inactive crystalline MoO3 phase. Tentatively it is presumed that the lower activity of 6MoO3/HBEA is most probably due to the formation of hardly accessible MoOx species located in the microporous channels. In order to achieve a more active and stable catalyst for the ISOMET of 1-hexene with ethylene, molybdena was loaded onto a gamma-alumina support (12MoO3/Al2O3), because at 12 wt% loading only highly dispersed MoO3 is formed. Further experiments were performed with a mixed bed of 12MoO3/Al2O3 (50 %) and zeolite HBEA (50 %) catalysts.

### 1-Hexene ISOMET using 12MoO3/Al2O3 and HBEA catalyst mixture

The activity and stability of the physical mixture of 12MoO3/Al2O3 and HBEA was studied in the ISOMET reaction of 1-hexene at 75 °C, ethylene pressure of 3 bar and, 6 and 12 gcat·E1-h-1 h space time (Fig. 8A and A'; B and B') and compared with MoO3/HBEA. In these experiments, we compared the properties of catalysts with the same molybdena content but different weights, i.e., a mixture of 1 g of 12MoO3/Al2O3 and 1 g of HBEA as well as 1 g of 13MoO3/HBEA. Over the freshly activated catalyst, the propylene yield was 33 % after 0.5 h of TOS. However, after reactivation of the catalyst the propylene yield more than doubled and reached a level of nearly 80 %.

### Table 2

| Catalyst       | TOS (h) | Propylene Yield (%) |
|----------------|---------|---------------------|
|                |         | Activated<sup>a</sup> | Reactivated<sup>a</sup> |
| 75             | 0.5     | 10                  | 20                      |
|                | 3       | 6                   | 16                      |
| 100            | 0.5     | 15                  | 59                      |
|                | 3       | 12                  | 19                      |
| 125            | 0.5     | 29                  | 86                      |
|                | 3       | 5                   | 17                      |
| 150            | 0.5     | 19                  | 82                      |
|                | 3       | 1                   | 10                      |

<sup>a</sup> Activation: The ex-situ calcined catalyst was in-situ pre-treated in a flow of Ar [50 ml min<sup>-1</sup>] at 550 °C for 2 h. The activated catalyst was cooled to the target temperature in a flow of Ar and the ISOMET reaction was performed.

<sup>b</sup> Reactivation: After 3 h of TOS, the reactant feed was stopped, the total pressure was reduced to atmospheric pressure. The catalyst was purged with a flow of Ar [50 ml min<sup>-1</sup>] for 30 min at the reaction temperature to remove olefins, then heated to 550 °C at a ramp rate of 10 °C min<sup>-1</sup> and maintained at this temperature for 2 h. The reactivated catalyst thus obtained was cooled to the target temperature in a flow of Ar and the ISOMET reaction was performed again.

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At 75 °C the activity of the two catalysts were about the same, but as the temperature increased, the propylene yield on 6MoO3/HBEA hardly changed. The number of active sites is presumably decreasing during the reaction as carbonaceous deposits may gradually block the micropores, thus the reactants molecules cannot access the active sites located inside the pores. Not only coking, but also the low oxidation state of Mo is also a reason of the decreased activity (vide infra).

To reactivate catalysts the Brønsted acid sites of HBEA zeolite support protonate the 2-hexene to form the carbenium ion intermediate of double bound isomerization.77-79 Zhang et al.11 reported that both the number of Brønsted acid sites and the high dispersion of MoO3 species has an important role in determining the OM activity.

Brønsted acid sites not only catalyse double-bond isomerization of alpha-olefins, but are also involved in the OM reactions, i.e., participate in the generation of active metal carbene species, which are the active site of the OM reactions. Previous work suggested that Brønsted acid OH groups interact with adjacent metal oxides, for example, MoOx, WOx, or ReOx for the generation of OM active carbene species.80,81 Recent results showed that using MoO3/SBA-15 catalyst, surface Brønsted acidic OHs coordinated to Mo(VI) protonate propylene and isopropoxide species are formed upon propylene adsorption.82 Such species are further oxidized by lattice oxygen of MoOx, to gas-phase acetone yielding reduced Mo(IV). This species reacts with gas-phase propylene to form the OM active Mo(VI)-alkylidene species. When Brønsted acid sites and MoOx species were located on the microporous support, rapid deactivation occurred during the ISOMET reaction.

The complementary characterization techniques revealed that in the 13MoO3/HBEA sample Mo exists in highly dispersed tetrahedral and polymerized octahedral MoOx species, which are active in the OM reaction. However, a fraction of Mo is present as catalytically inactive crystalline MoO3 phase. Tentatively it is presumed that the lower activity of 6MoO3/HBEA is most probably due to the formation of hardly accessible MoOx species located in the microporous channels. In order to achieve a more active and stable catalyst for the ISOMET of 1-hexene with ethylene, molybdena was loaded onto a gamma-alumina support (12MoO3/Al2O3), because at 12 wt% loading only highly dispersed MoO3 is formed. Further experiments were performed with a mixed bed of 12MoO3/Al2O3 (50 %) and zeolite HBEA (50 %) catalysts.

### 1-Hexene ISOMET using 12MoO3/Al2O3 and HBEA catalyst mixture

The activity and stability of the physical mixture of 12MoO3/Al2O3 and HBEA was studied in the ISOMET reaction of 1-hexene at 75 °C, ethylene pressure of 3 bar and, 6 and 12 gcat·E1-h-1 h space time (Fig. 8A and A'; B and B') and compared with MoO3/HBEA. In these experiments, we compared the properties of catalysts with the same molybdena content but different weights, i.e., a mixture of 1 g of 12MoO3/Al2O3 and 1 g of HBEA as well as 1 g of 13MoO3/HBEA. Over the freshly activated catalyst, the propylene yield was 33 % after 0.5 h of TOS. However, after reactivation of the catalyst the propylene yield more than doubled and reached a level of nearly 80 %.
Repeated reactivation gave similar high propylene yield (Fig. 8). Not only the initial activity of the catalyst improved significantly but the lifetime of the catalyst also increased. (Fig. 8A and A'). The propylene yield on the activated catalyst mixture decreased from 33 to 18 % in 3 h of TOS. Deactivation of the reactivated catalyst is slower, the propylene yield dropped from 79 only to 57 % in 3 h. Significantly lower initial activity and faster deactivation were observed for 13MoO$_3$/HBEA (Table 2). Over the activated and reactivated 13MoO$_3$/HBEA catalyst in three hours of TOS the propylene yield decreased from 10 to 6 % and 20 to 16 %, respectively. The higher activity of the 12MoO$_2$/Al$_2$O$_3$ catalyst compared to 13MoO$_3$/HBEA is due to the higher concentration of active MoO$_3$ species on alumina than on zeolite (microporous aluminosilicate) confirmed by XRD, Raman and UV-VIS spectroscopies. Higher space time resulted in a significantly higher propylene yield. The catalyst reactivation has shown significantly higher (>90%) propylene yield and longer catalyst lifetime (Fig. 8B and B').

Further experiments have been carried out to investigate the influence of the reaction temperature on the overall propylene yield (Fig. 9). At 125 °C, the propylene yield was around 50 %. The catalyst activity did not change as a function of TOS. After reactivation of the catalyst, a propylene yield of more than 90 % can be obtained. Some catalyst deactivation was observed, however after 3 h TOS still 80 % propylene yield could be measured.

By increasing the reaction temperature up to 150 °C even higher yield and longer catalyst lifetime was observed. After the catalyst reactivation approximately 100 % propylene yield was found, which was maintained up to two hours. From the third hour of the reaction the propylene yield slightly decreased, however it was still high (> 80%). As it was observed after the first run and catalyst reactivation, the catalyst performance was always significantly higher.

**Activation and reactivation of 12MoO$_2$/Al$_2$O$_3$ and HBEA catalyst mixture**

Conventional pre-treatment of the heterogeneous OM catalysts includes high-temperature calcination and inert gas purging. It has also been shown that olefin pre-treatment at low or high temperatures can improve the initial activity. Amakawa et al. reported that heat treatment in inert gas at 550 °C for 2 hours after the room-temperature olefin adsorption doubled the catalytic activity of MoO$_2$/SBA-15. Surface isopropoxide species were supposed to form and activate surface Mo(VI) sites by reduction to Mo(IV) and formation of C$_3$ oxygenate (acetone). This reduced Mo species react with propylene and gives active Mo(VI)-allylidene species. Two orders of magnitude increase in activity was observed over silica-supported MoO$_3$ and WO$_3$ when propylene adsorption was performed at high temperature, 550 °C and 700 °C, respectively. The high-temperature activation was explained by Pseudo-Wittig mechanism.
0.5 h and cooled down to the reaction temperature. Maintained at this temperature for 2 h, and then purged with Ar (50 ml min⁻¹). Ar-activation ethylene was fed into the reactor for 1 h at 75 °C then changed to Ar.

Hexene ISOMET the catalyst was purged in a flow of O₂ (50 ml min⁻¹). After 3 h of TOS, the ISOMET reaction was stopped (Fig. 10). The propylene yield was about 15 %.

Higher propylene yield (~ 28 %) was obtained over Ar-activated catalyst (Figs. 8 and 10). However, performing ISOMET reaction for 3 of TOS and treatment again in inert gas flow at 550 °C for 2 h, improved activity was observed. The propylene yield increased to 80 %. When the catalyst was reactivated in O₂ flow at 550 °C for 1 h followed by purging with Ar flow for 2 h no catalyst activity improvement was observed. It remained the same as those of the Ar-activated catalyst.

Reactivation in O₂ or Ar flow at 550 °C increased the propylene yield. When the catalyst was reactivated in O₂ flow at 550 °C for 1 h followed by purging with Ar flow for 2 h no catalyst activity improvement was observed. It remained the same as those of the Ar-activated catalyst.

Reactivation in Ar flow at 550 °C and HBEA mixture oxidized in-situ at 550 °C confirming that surface Mo(VI) oxide species are not active in OM reaction. The experiment was stopped after 0.5 h of TOS, not waiting for the catalyst to be activated in-situ during the reaction, as it was proved by Amakawa et al. 20

The catalyst pretreated in 5% H₂/Ar mixture at 550 °C for 2 h has the lowest activity (Figs. 10 and S8). At 75 °C and 3 bar ethylene pressure the propylene yield was about 15 %. Higher propylene yield (~ 28 %) was obtained over Ar-activated catalyst. The propylene yield increased to 80 %. When the catalyst was reactivated in O₂ flow at 550 °C for 1 h followed by purging with Ar flow for 2 h no catalyst activity improvement was observed. It remained the same as those of the Ar-activated catalyst.

The propylene yield increased to 80 %. When the catalyst was reactivated in O₂ flow at 550 °C for 1 h followed by purging with Ar flow for 2 h no catalyst activity improvement was observed. It remained the same as those of the Ar-activated catalyst. Fig 10 shows that improved ISOMET activity was also observed when only the cross-coupling agent, ethylene was fed into the reactor at 75 °C (actually self-metathesis proceeds) and the catalyst was heat-treated in Ar at 550 °C (ethylene-activated catalyst). These results suggest that after 1-hexene ISOMET or ethylene OM, during the Ar-reactivation the remaining olefins may participate in the generation of the catalytically active molybdenum species also. 33 Calcined the catalyst in O₂ flow at 550 °C Mo-carbene species are decomposed and Mo is oxidized to Mo(VI).

The XPS results shows that during inert gas treatment at 550 °C part of Mo(VI) are reduced to Mo(V) species. The ethylene-activated catalyst contains more Mo(V) species. The high catalyst performance can also be explained by the partial reduction of Mo initiated by the hydrocarbon residues remaining on the catalyst surface.

Propylene Synthesis via ISOMET of FCC fractions using 12MoO₃/Al₂O₃ and HBEA catalyst mixture

Our further aim was to develop OM based chemical process for a mixture produced by FCC cracking (further named as crude FCC and FCC light). The analysis of FCC light and FCC fractions revealed that the olefin content is about 37 wt% in FCC light and 22 wt% in crude FCC and approximately 50 % of the olefins are 2-olefins (Fig. S10). The main olefin components of FCC light fraction are C₅-C₇ olefins, however some C₄ and C₈ components could also be detected. Experiments have been carried out to synthetize propylene from crude FCC fraction. Theoretically, regardless of the nature of the linear mono olefins (either terminal or internal) all olefins can be converted to propylene via ISOMET using ethylene (Scheme 1). In terms of
weight of olefins approximately 100 tons of C4–C8 olefin mixture can be converted to 200 tons of propylene by using 100 tons ethylene.

The ISOMET of FCC light and FCC fractions were carried out without any pretreatment at 75 °C and 3 bar ethylene pressure. The FCC light fraction containing mainly CS-C7 olefin components. Due to the relatively high olefin content (35–37%) and purity, high propylene yield (70 %) and long catalyst lifetime have been reached (Fig. 11). Following the reactivation significantly higher (90 %) propylene yield and longer catalyst lifetime were observed. After 8 hours of TOS the catalyst remained still active and the propylene yield achieved 50 %. Compared to the 12MoO₃/Al₂O₃ – HBEA catalyst mixture significantly lower propylene yield could be obtained using the 12MoO₃/HBEA catalyst (Fig. S11).

The ISOMET of FCC shows that after 0.5 h TOS slightly higher than 45 % propylene yield have been obtained, which has been declining steadily in the next two hours (Fig. 11). The catalyst reusability was also investigated. It was found that experiments carried out with reactivated catalyst resulted in significantly higher (75%) propylene yield and longer catalyst lifetime.

Experimental

Catalyst preparation

MoO₃/Al₂O₃ olefin MET catalyst was prepared by incipient wetness impregnation of the alumina support. Commercial γ-Al₂O₃ (Ketjen, CN 300) was first calcined at 500 °C for 8 h (at a heating rate of 10 °C min⁻¹) and then impregnated with ammonium heptamolybdate solution. The sample was air-dried at 120 °C for 6 h and then slowly heated (2 °C min⁻¹) to 500 °C and kept at this temperature for 12 h. The MoO₃ content of the air-calcined catalyst was 11.7 wt%, so the catalyst is designated as 12MoO₃/Al₂O₃.

MoO₃/HBEA ISOMET catalysts were prepared by wet impregnation of H-Beta (HBEA; Si/Al=12; SÜD-Chemie AG; München) with ammonium heptamolybdate solution. Before impregnation zeolite HBEA was calcined at 500 °C for 8 h. After impregnation, the solvent was evaporated by keeping the sample at 120 °C for 6 h. The samples were then heated to 500 °C in air and kept at this temperature for 12 h. The air-calcined samples are designated as xMoO₃/HBEA. The MoO₃ content of the catalysts were 13.5 and 6.1 wt%.

Catalyst characterization

X-ray powder diffraction patterns of the catalysts were determined using Transmission Fourier-transform infrared (FT-IR) spectra of the adsorbed pyridine (Py) on Brønsted- and/or Lewis acid sites of the catalysts. IR spectra of the sample were recorded at room temperature averaging 32 scans at a resolution of 2 cm⁻¹. Spectra were normalized to a wafer thickness of 5 mg/cm². Difference spectra of adsorbed Py were generated by subtracting the spectrum of the wafer before pyridine adsorption from the spectrum of the wafer loaded by pyridine.

The in-situ UV/Vis spectra were collected by Thermo Scientific Evolution 300 UV/VIS spectrophotometer equipped with Praying Mantis Diffuse Reflectance Accessory and High Temperature and Pressure Reaction Chamber. The catalysts were diluted 50-50 wt% with BaSO₄.

Raman analyses were carried out at the Research and Industrial Relations Center of the Faculty of Science, Eötvös Loránd University of Budapest, using a HORIBA JobinYvon LabRAM HR 800 Raman microspectrometer. A frequency doubled Nd-YAG green laser with a 532 nm excitation wavelength was employed, displaying 10-20 mW on the sample surface. An OLYMPUS ×50 objective was used to focus the laser. For Raman analyses 100 μm focal hole, 600 grooves/mm optical grating, 20-120 s cumulated exposition time were used. The spectral resolution of measurements was 3.0 cm⁻¹.

The XPS measurements - using self-supported wafers - were performed by using an Omicron EC 125 electron spectrometer in the “Fixed Analyser Transmission” mode; photoelectrons were excited by non-monochromatized MgKα (1253.6 eV) radiation. Detailed spectra were recorded with a “Pass energy” of 30 eV, providing resolution around 1 eV. Spectra were collected in the “as received” state of the catalysts, after 2 h annealing in 300 mbar Ar at 550°C (simulated activation), after 3 h exposure to 100 mbar C₃H₄ around 100°C (simulated reaction) and after repeated activation at 550°C. The treatments were performed in a preparation chamber attached to the electron spectrometer so no exposure to atmosphere was needed during sample transfer. Spectra were processed with the CasaXPS package [N. Fairley, “CasaXPS: Spectrum Processing Software for XPS, AES and SIMS,” Cheshire, 2006, http://www.casaxps.com], while quantitative evaluation of the data was performed with the XPSMultiQuant package [M. Mohai, “XPS MultiQuant: Multimodel XPS Quantification Software,” Surf. Interface Anal. 36 (2004) 828–832, M. Mohai, “XPS MultiQuant: Multi-model X-ray photoelectron spectroscopy quantification program,” 2011, http://
http://aki.ttk.hu/XMQpages/XMQhome.php]. As the samples were insulating, charge compensation was performed by setting the binding energy of the main C 1s peak (arising from adventitious hydrocarbon) of the “as received” catalysts to 285.0 eV.

Catalytic test
The catalytic experiments were carried out in a down-stream, fixed-bed, and stainless-steel tube reactor (12 mm ID). The reactor was loaded with 2 g of catalyst grains prepared by compression of the sample powder, crushing and sieving (0.315–0.63 mm) and flow rate of reactant liquid mixture (1,5-6 ml/h) were varied. The reactor temperature was controlled by an Omron ESCN controller. The liquid mixture (1-hexene in hexane solution (30%), FCC, FCC light) was fed into the reactor by high-pressure micro pump (Teledyne Isco, Model 100DM). The gas was introduced by mass flow controller (Aalborg GCFC17). The total pressure and the reaction temperature were varied in the range of 1-50 bar and 25-150 °C, respectively. Using water cooling, the reactor effluent was separated to liquid and gas products. The liquid product mixtures were analysed by GC-MS (Shimadzu QP-2010) using a 60 m ZB-WAX PLUS capillary column. The gaseous reactor effluent was analysed for detection of propylene and light hydrocarbons using an on-line gas chromatograph (Varian 3300) with flame ionization detector (FID) and applying 30 m Supelco (alumina/chloride) capillary column. The propylene yield as outcome parameter was determined, in some cases complete mass balance, and including the quantitative distribution of the intermediate species has been calculated.

Catalyst activation/reactivation
Activation and reactivation of the catalysts were performed in inert gas (Ar) flow at 550 °C for 2h. Activation: the ex-situ calcined catalysts were in-situ pre-treated in a flow of Ar (50 ml min⁻¹), at atmospheric pressure, at 550 °C for 2 h. The activated catalyst was cooled to the target temperature in a flow of Ar and the ISOMET reaction was performed. Reactivation: after 3 h of TOS, the reactant feed was stopped and the catalyst was purged with a flow of Ar (50 ml min⁻¹) for 30 min at reaction temperatures and atmospheric pressure. Then it was heated to 550 °C at a ramp rate of 10 °C min⁻¹ and maintained at this temperature for 2 h. The reactivated catalyst thus obtained was cooled to the target temperature in a flow of Ar and the ISOMET reaction was performed again. After ISOMET reaction, the catalyst was purged with Ar flow at 75 °C for 0.5 h and the effluent was analysed by GC-MS. It was found that the reactant and the intermediate olefins (ethylene, propylene, butenes, pentenes and hexenes) completely desorbed from the catalyst surface within 30 min. Increasing the temperature longer olefins/paraffins (>C6) were detected by GC-MS. Above 300 °C there was no any further organic species observed.

General procedure for isomerization with HBEA.
The isomerization catalyst (HBEA) was pre-treated in-situ in Ar (50 ml/min) flow in the reactor at atmospheric pressure and 450 °C for 2 h. After catalyst pre-treatment the reactor was cooled to the target temperature under Ar flow. The isomerization of 1-hexene was investigated at the temperature range of 75-150 °C, 6 g cat g₁-hexene⁻¹ h space time in Ar flow at atmospheric pressure.

General procedure for ethenolysis. After catalyst pre-treatment the reactor was cooled to the target temperature under Ar flow, and then pressurized to the target pressure with ethylene. The ethenolysis of the reactants were investigated at different temperatures (25-150 °C), pressure (1-50 bar) and space time (6-12 g cat g₁-reactant⁻¹ h). The ethylene/1-hexene molar ratio was 10.

Conclusions
Heterogeneous molybdena catalysts were prepared using alumina, and zeolite beta (HBEA) as support. The catalysts and their mixtures thereof were characterized and studied in the ISOMET of 1-hexene and FCC olefins. It was shown that the Brønsted sites of HBEA catalyze the double bond isomerization, meanwhile the MoO₃ species supported on alumina or HBEA are active in the ethenolysis of olefins to give propylene as final product from both 1-hexene and FCC olefins. Over a mixture of 12MoO₃/Al₂O₃ and HBEA catalysts quantitative conversion of 1-hexene to propylene could be achieved at 150 °C, 3 bar ethylene pressure and 6 g cat g₁-hexene⁻¹ h space time. The catalyst mixture had also good performance in the ethenolysis of FCC olefins. Relative to the 12MoO₃/Al₂O₃ – HBEA system, the 13MoO₃/HBEA catalyst has rendered lower activity and significantly shorter catalyst lifetime presumably due to the lower amount of highly dispersed MoO₃ sites formed on the zeolite.

The deactivated ISOMET catalyst system could be reactivated by treatment in argon flow at 550 °C for 2 hours. The reactivated catalysts showed higher initial activity and stability than the fresh catalysts pre-treated in the same way. It has been demonstrated that treatment of the catalyst with olefins such as ethylene before inert gas activation resulted in significant catalyst activity improvement. It indicates that the adsorbed olefins may play key role in the formation of active metal centers during the catalyst reactivation process. Activating the catalyst either in strongly reducing or oxidizing environment, however led to the loss of activity.

Conflicts of interest
There are no conflicts to declare.

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