

## Propene yield enhancement from metathesis of ethene and 2-butene on mixed HBeta-alumina supported molybdenum-based catalysts using aluminum nitrate as alumina precursor

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The mixed HBeta-alumina supported molybdenum-based catalysts with 4 wt% Mo loading were prepared by incipient wetness impregnation method. Aluminum nitrate and aluminum oxide were used as alumina precursors in mixing with HBeta zeolite followed by calcination at 550°C. The catalyst using aluminum nitrate as alumina precursor, Mo/AN+HB(550), markedly outperformed its counterpart using aluminum oxide as precursor, Mo/AO+HB(550), in both 2-butene conversion and propene selectivity from metathesis of ethene and 2-butene. The relatively higher metal-support interaction, as well as the derivation of surface tetrahedral molybdenum oxide species were discernible on Mo/AN+HB(550), as observed from H<sub>2</sub>-TPR and UV-vis spectra, respectively. In addition, the higher acidity obtained on Mo/AN+HB(550), presumably due to the better protection of HBeta zeolite structure achieved by the optimum compatibility between Al using aluminum nitrate as alumina precursor and HBeta, was believed to play a significant role for the enhancement of propene yield by metathesis of ethene and 2-butene.

**Keywords:** Aluminum nitrate; Molybdenum-based catalyst; Metathesis; Propene

### INTRODUCTION

Metathesis reaction of ethene and 2-butene is an alternative way to produce propene, the demand of which is rapidly increasing on the worldwide market. In this way the C<sub>4</sub> alkenes from the refineries and steam crackers can be upgraded [1–4]. The catalysts used for such reaction are mostly based on rhenium, molybdenum and tungsten [5]. Though rhenium-based catalysts supported on alumina or silica-alumina are the most interesting ones due to their high activity even at room temperature, the costs of rhenium compounds are high and catalysts with low rhenium loadings have only negligible activities [6]. Supported molybdenum oxide catalysts have received much attention, as they are widely used in petrochemical processes including metathesis of alkenes [6]. Liu *et al.* [6] have found that the supported Mo/HBeta catalysts show some activities for the olefin metathesis; however, the catalytic performance remarkably increases after addition of Al<sub>2</sub>O<sub>3</sub>. Moreover, they have reported that a molybdenum-based catalyst impregnated on HBeta-Al<sub>2</sub>O<sub>3</sub>(Mo/HB–Al<sub>2</sub>O<sub>3</sub>) with an optimum Mo loading

of 4 wt% was the best catalyst for the metathesis of ethene and 2-butene to propene among the catalysts evaluated, namely, Mo/MgO, Mo/Al<sub>2</sub>O<sub>3</sub>, Mo/MCM-22, Mo/ZSM-35, Mo/silicate and 6Mo/SAPO-11 [5, 7]. The relatively poor metathesis activity of Mo/HBeta without Al<sub>2</sub>O<sub>3</sub> was ascribed to the possible dealumination of framework Al in HBeta upon the high loading of Mo [8]. Though alumina addition into the composite support has been proposed to protect the framework of HBeta from being destroyed upon Mo loadings to a large extent due to the preferential migration of Mo species on the alumina surface [9, 10], the synergistic effect of alumina precursor on the metathesis activity has not yet been observed.

Therefore, this work aims at investigating the enhancement of propene production by metathesis of ethene and 2-butene on mixed HBeta-alumina supported molybdenum-based catalyst by adopting aluminum nitrate as a precursor for alumina. All catalysts were prepared by incipient wetness impregnation of 4 wt % of molybdenum on a mixed HBeta-alumina support. The catalyst characterization was conducted by employing techniques of BET surface area assessment, X-Ray diffraction, NH<sub>3</sub>-TPD, UV-vis spectra and H<sub>2</sub>-TPR.

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## EXPERIMENTAL

### 2.1 Preparation of catalysts

HBeta zeolite (Si/Al = 27) manufactured by Tosoh Corporation physically mixed with either aluminum nitrate nonahydrate ( $\text{AlN}_3\text{O}_3 \cdot 9\text{H}_2\text{O}$ , Fluka) or aluminum oxide (Fluka) was used as a support with HBeta/Al-precursor ratio of 70:30. The mixed support samples were calcined in air at predetermined temperatures ranging from 350–950 °C for 2 h before impregnation with an aqueous solution of ammonium molybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_6\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) to obtain 4 wt% of molybdenum. The catalysts were designated as Mo/AN+HB(y) and Mo/AO+HB(y) for the samples prepared from the support of HBeta mixed with aluminum nitrate and aluminum oxide, respectively. After impregnation, all catalysts were calcined in air at 680°C for 2 h.

### 2.2 Catalyst characterization

X-ray diffraction patterns of all catalysts were collected on an X-ray diffractometer (Siemens D5000) using Ni filters Cu  $K\alpha$  radiation from 20° to 80°.

Brunauer-Emmett-Teller (BET) surface areas, as well as the pore volumes of the catalysts were obtained on a surface area analyzer (Micromeritics ASAP 2010).

The catalyst reducibility was assessed by temperature programmed reduction with hydrogen ( $\text{H}_2$ -TPR). A portion of 0.2 g of the catalyst sample was placed in a quartz tube and pretreated in Ar flow (50 ml/min) at 200°C for 2 h. Then the carrier gas was replaced with 10%  $\text{H}_2$  at the same flow rate and was balanced with Ar in the temperature range of 40 to 800°C. The peak area assessment was made by a Micromeritics Chemisorb 2750 automated system supplied with Chemi Soft TPx software.

The catalyst acidity was determined by the technique of ammonia temperature programmed desorption ( $\text{NH}_3$ -TPD). A portion of 0.2 g of the catalyst sample was placed in a quartz tube and was pretreated in helium flow (50 ml/min) at 200°C for 2 h. Then, the catalyst sample was adsorbed till saturation with 15%  $\text{NH}_3$  balanced with He. The physisorbed ammonia was desorbed in a helium gas flow for about 1 h. The sample was subsequently

heated from 40 to 800°C at a heating rate of 10°C/min. The peak area assessment was made by a Micromeritics Chemisorb 2750 automated system supplied with Chemi Soft TPx software.

UV-vis spectra were recorded on a Lambda 650 UV-vis spectrometer equipped with a diffuse reflectance attachment at room temperature in the range of 200–900 nm.

### 2.3 Catalytic performance for metathesis reaction

A portion of 2.0 g of catalyst was placed in a fixed bed reactor with inner diameter (ID) of 7.5 mm to which a type K thermocouple was mounted. The catalyst was pretreated at 550°C with a heating rate of 10°C/min in a nitrogen flow for 1 h and was cooled down to reaction temperature of 120°C (pressure=0.1MPa). The feed consisting of 4%  $\text{C}_2\text{H}_4$ , 2% *trans*-2- $\text{C}_4\text{H}_8$  balanced with  $\text{N}_2$  (equivalent to  $\text{C}_2\text{H}_4$ /*trans*-2- $\text{C}_4\text{H}_8$  ratio of 2:1) was used. The sample analysis was performed on a Shimadzu GC 2014 gas chromatograph equipped with a column of packed 10% silicone SE-30 (3.02 m with 0.53 mm ID) and a flame ionization detector using nitrogen as the carrier gas (5 ml/min).

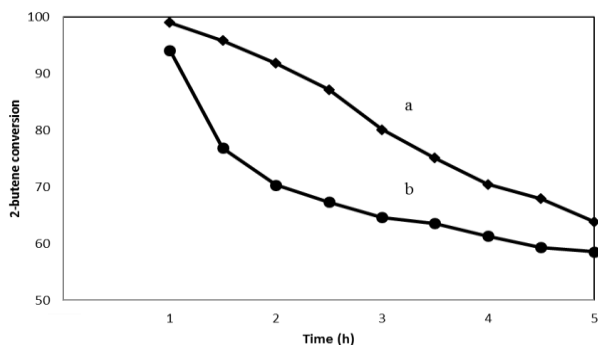
## RESULTS

The physical properties of the molybdenum-based catalysts impregnated on mixed HBeta and aluminum oxide calcined at 550°C, Mo/AO+HB(550), and mixed HBeta and aluminum nitrate calcined at the same temperature, Mo/AN+HB(550), are shown in Table 1.

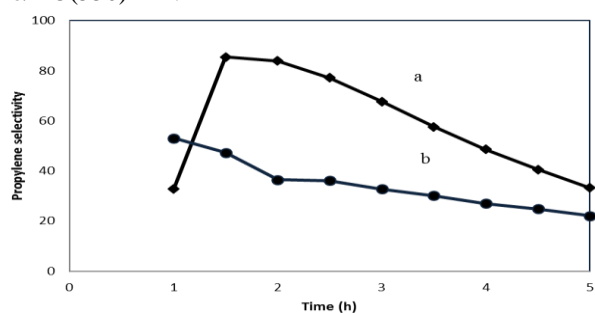
No significant difference in pore volume was observed for both samples, while the BET surface areas and pore sizes of both samples were in the range of 412–423  $\text{m}^2/\text{g}$  and 6.38–8.64 nm, respectively. The relative crystallinity of Mo/AN+HB(550) was slightly higher than that of Mo/AO+HB(550). The conversions of 2-butene and propene selectivities for the metathesis reaction of ethene and 2-butene on Mo/AN+HB(550) and Mo/AO+HB(550) are shown in Figs. 1 and 2, respectively. It is clearly seen that Mo/AN+HB(550) using aluminum nitrate as a precursor markedly outperformed its counterpart using aluminum oxide as a precursor,

**Table 1.** Physical properties of catalysts prepared with different Al-precursors.

Sample	4%Mo/AIO(550)-HB	4%Mo/AIN(550)-HB
BET surface area ( $\text{m}^2/\text{g}$ )	423	412
Pore volume ( $\text{cm}^3/\text{g}$ )	0.40	0.38
Pore size (nm)	6.38	8.64
Relative crystallinity (%)	51	55



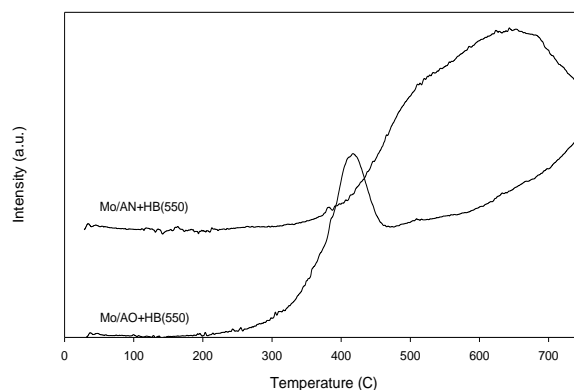
**Fig.1.** Metathesis conversion on mixed support molybdenum-based catalysts using different Al-precursors. (a) = Mo/AN(550)-HB and (b) = Mo/AO(550)-HB.



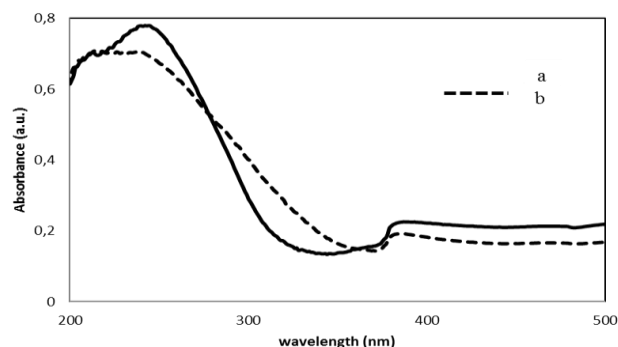
**Fig.2.** Metathesis selectivity on mixed support molybdenum-based catalysts using different Al-precursors. (a) = Mo/AN(550)-HB and (b) = Mo/AO(550)-HB

Mo/AO+HB(550), in both 2-butene conversion and propene selectivity throughout the observed 5 h on stream. This reflects the different interaction characteristics between Al and HBeta obtained using different Al precursors and hence the different metal-support interaction characteristics obtained on both catalyst samples. The H<sub>2</sub>-TPR profiles of both catalyst samples are shown in Fig. 3. The Mo/AO+HB(550) catalyst displayed an H<sub>2</sub>-TPR peak at about 400°C while a relatively broader peak at higher temperature (around 500 to 600°C) was observed for the Mo/AN+HB(550) catalyst.

The stronger metal-support interaction obtained on the catalyst sample using aluminum nitrate as Al precursor might be responsible, among the other things, for the better catalyst performance on metathesis reaction. Fig. 4 shows the UV-vis spectra of both catalyst samples. The relatively strong peak around 230 nm corresponding to the surface tetrahedral Mo oxide species [1] was clearly observed on the catalyst sample using aluminum nitrate as Al precursor. This should be responsible for the improved metathesis activity of Mo/AN+HB(550) favored by the existence of surface tetrahedral active sites. As shown in Fig. 5, the



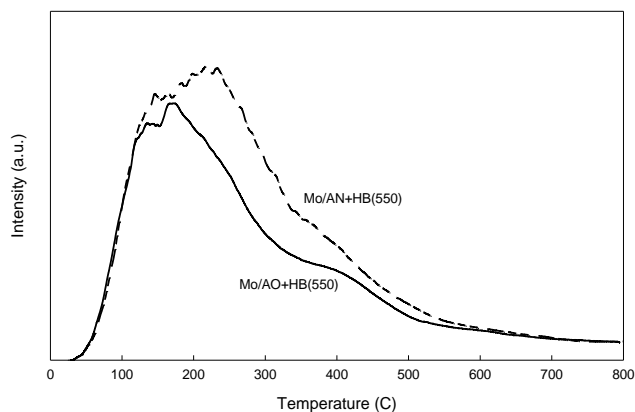
**Fig.3.** H<sub>2</sub>-TPR profiles for mixed support molybdenum-based catalysts using different Al-precursors.



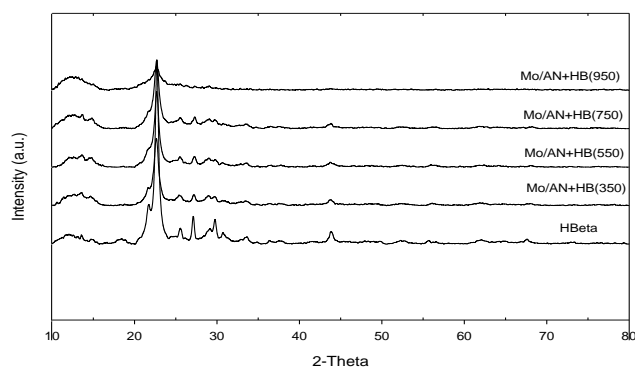
**Fig.4.** UV-vis spectra of mixed support molybdenum-based catalysts using different Al-precursors. (a)= Mo/AN(550)-HB, (b)= Mo/AO(550)-HB.

NH<sub>3</sub>-TPD profiles of both catalyst samples reveal that Mo/AN+HB(550) displays higher acidity than its counterpart, Mo/AO+HB(550). The Brønsted acid-derived surface hydroxyl group was believed to react with molybdenum oxide crystallites, from which the metathesis active site of surface tetrahedral molybdenum oxide species could be obtained. Phongsawat *et al.* [11] have studied the metathesis of ethylene and 2-pentene for propylene production on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported rhenium catalysts. They have found that the weak acidity equivalent to the NH<sub>3</sub>-TPD profile at around 300°C or lower was not strong enough for isomerization reaction and metathesis activity to be maintained. Therefore, the acid strength in this case was supposed to be moderate enough to promote metathesis activity essentially without significant contribution to isomerization. This should be one of the factors that promote the enhancement of propene production by metathesis reaction.

Catalyst heat treatment may somewhat influence the thermal stability of the support structure which may affect the catalytic performance. Therefore, the calcination temperatures of mixed HBeta and alumina, using aluminum nitrate as a precursor,

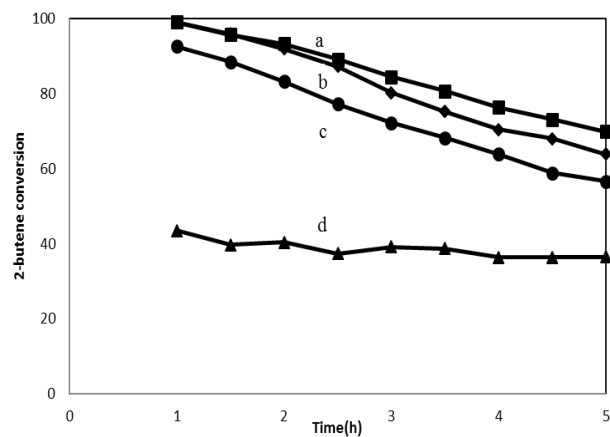


**Fig.5.** NH<sub>3</sub>-TPD profiles for mixed support molybdenum-based catalysts using different Al-precursors.

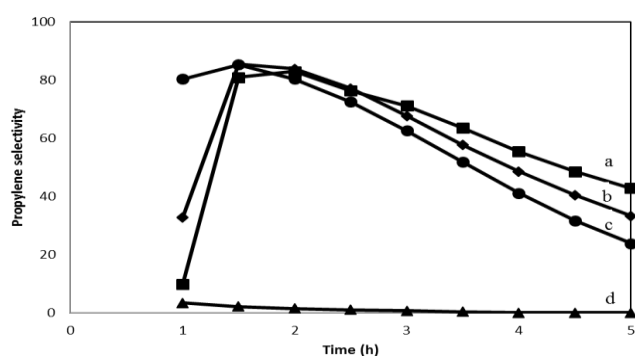


**Fig.6.** X-ray diffraction pattern of mixed support molybdenum-based catalysts using different Al-precursors calcined at different temperatures.

were varied from 350 to 950°C. The XRD patterns of the catalysts calcined at different temperatures are shown in Fig. 6. The characteristic peaks of HBeta zeolite were observed for all catalysts due to the amorphous characteristics of alumina. It was found that the crystallinity of the catalysts markedly decreased at calcination temperatures higher than 750°C. The structural collapse of HBeta zeolite may occur at high calcination temperature especially for the catalyst calcined at 950°C designated as Mo/AN+HB(950). The conversion of 2-butene and propene selectivity by metathesis reaction on those catalysts calcined at different temperatures are demonstrated in Figs. 7 and 8, respectively. The catalyst performance on both 2-butene conversion and propene selectivity deteriorated with the higher calcination temperatures during the 5 h on stream. The adverse effect of high calcination temperature was evidently most pronounced on the catalyst calcined at 950°C with almost no propene formed on Mo/AN+HB(950) even at the early period of reaction. This may be attributed to the structural collapse of HBeta zeolite at such high temperature



**Fig.7.** Metathesis conversion on mixed support molybdenum-based catalysts using different Al-precursors calcined at different temperatures. (a) = Mo/AN(350)-HB, (b) = Mo/AN(550)-HB, (c) = Mo/AN(750)-HB, and (d) = Mo/AN(950)-HB.



**Fig.8.** Metathesis selectivity on mixed support molybdenum-based catalysts using different Al-precursors calcined at different temperatures. (a) = Mo/AN(350)-HB, (b) = Mo/AN(550)-HB, (c) = Mo/AN(750)-HB, and (d) = Mo/AN(950)-HB.

as evidenced by the considerably low crystallinity on its XRD pattern.

## DISCUSSIONS

The significantly low metathesis activity of Mo/AN+HB calcined at 950°C due to structural collapse of HBeta is analogous to the adverse effect of dealumination derived at high Mo loading contents in Mo/HBeta without alumina addition, as found by Liu *et al.* [6]. According to Liu *et al.* [10], the HBeta particles were surrounded by irregular alumina floccules as observed from high-resolution SEM images. The preferential distribution of Mo species in alumina rather than in HBeta, as observed from the quantitative EDS analysis using aluminum nitrate as precursor of alumina, may contribute to the better formation of Al floccules with HBeta which favors the preferential migration of Mo in the alumina surface. As a consequence, better protection of the HBeta structure by alumina using aluminum nitrate as a precursor and hence

higher acidity contributing to the good metathesis activity of propene formation from ethene and 2-butene might be achieved. Though the precise role of aluminum nitrate as alumina precursor on the enhancement of propene production is subject to further investigation, we are strongly convinced that the optimum compatibility between Al and HBeta is the key factor to obtain an active catalyst for metathesis reaction with the acquisition of optimum metal-support interaction and Brønsted acidity. Our further work to modify the mixing of Al and HBeta by adopting sol-gel preparation is under investigation and the preliminary results seem to support our expectation.

### CONCLUSIONS

The mixed HBeta-alumina supported molybdenum catalyst calcined at 550°C using aluminum nitrate as a precursor, Mo/AN+HB(550), markedly outperformed its counterpart using aluminum oxide as a precursor, Mo/AO+HB(550), in both 2-butene conversion and propene selectivity throughout the observed 5 h on stream of metathesis reaction between ethene and 2-butene. The relatively stronger metal-support interaction on Mo/AN+HB(550), as observed from H<sub>2</sub>-TPR, as well as the derivation of surface tetrahedral molybdenum oxide species, as observed from UV-vis spectra should be, among other factors, responsible for the relatively good metathesis activity of the catalyst. The higher acidity acquired on Mo/AN+HB(550), probably due to the better protection of HBeta zeolite structure achieved by the optimum compatibility between Al using aluminum nitrate as precursor and HBeta, was believed to play a significant role for the enhancement of propene production by metathesis reaction of ethene and 2-butene.

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## УСКОРЯВАНЕ НА ПРЕВРЪЩАНЕТО НА ПРОПЕН ЧРЕЗ ПРЕГРУПИРАНЕ НА ЕТИЛЕН И 2-БУТЕН ВЪРХУ СМЕСЕН КАТАЛИЗАТОР НА ОСНОВАТА НА МОЛИБДЕН, НАНЕСЕН ВЪРХУ НВ-АЛУМИНИЕВ ТРИОКСИД, ПОЛУЧЕН ОТ АЛУМИНИЕВ НИТРАТ

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(Резюме)

Катализаторът, съдържащ 4% тегл. молибден се приготвя по метода на началното импрегниране с влага. Като прекурсори за получаването на подложката от алуминиев оксид се използват алуминиев нитрат и алуминиев триоксид. Те се смесват с НВ зеолит, след което сместа се калцинира при 550°C. Катализаторът Мо/АН+НВ(550), получен с алуминиев нитрат като прекурсор забележимо превъзхожда другия (Мо/АО+НВ(550)), при превръщането на 2-бутен и по отношение на селективността спрямо пропен при регрупирането на етилена и 2-бутена. Относително силните взаимодействия метал-подложка, както и получаването на повърхостни тетраедрични форми на молибденовия оксид са забележими при Мо/АН+НВ(550) и са установени с помощта на H<sub>2</sub>-TPR and UV-видими спектри. Освен това се приема, че високата киселинност, получена при Мо/АН+НВ(550) има значителна роля за ускоряването на регрупирането на етилена и 2-бутена до пропен. Вероятно това се дължи на по-добрата защита на НВ-зеолитната структура от алуминия, постигната при използването на алуминиев нитрат като прекурсор.