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Propylene metathesis over $Re_2O_7/Al_2O_3–B_2O_3$ catalysts

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A series of alumina aluminum borate (AAB) with various Al/B molar ratios were prepared by the coprecipitation method. The supported rhenium oxide catalysts with various contents of Re_2O_7 were also prepared by the impregnation method with perrhenic acid. The catalytic activity and stability of Re_2O_7/AAB catalysts for the reaction of propylene metathesis were tested in a fixed-bed microreactor. It was found that Re_2O_7/AAB is more active, stable and regenerable than Re_2O_7/Al_2O_3 for propylene metathesis. The optimum Al/B molar ratio was found to be in the range of 4–10.

Keywords: Propylene metathesis; alumina aluminum borate; rhenium oxide; temperature-programmed reduction (TPR); temperature-programmed desorption (TPD)

1. Introduction

Catalysts containing rhenium are well known for their high activity on olefin metathesis [1], hydrodesulfurization [2] and hydronitration [3], in comparison with Mo and W catalysts. Supported rhenium catalysts for the metathesis of alkene have been extensively studied in the past two decades [4,5]. Most of the studies deal with the catalyst Re_2O_7/Al_2O_3 [6–12], although other material such as SiO_2 or $SiO_2–Al_2O_3$ could also be used as the catalyst support [13,14]. The metathesis of propylene catalysed by rhenium oxide on alumina was first reported by researchers of British Petroleum [15].

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In this study we investigated the catalytic activity, selectivity and stability of propylene metathesis over the catalyst system $Re_2O_7/Al_2O_3-B_2O_3$. The preparation and characterization of the catalysts were also studied.

2. Experimental

Support preparation. The alumina aluminum borate (AAB) support was prepared from common solutions of aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) and boric acid (H_3BO_3) using an ammonium hydroxide solution as a precipitant. A well-stirred container was charged with distilled water. The previously described common solutions and ammonium hydroxide solution were slowly added to this distilled water with the rate of addition controlled in order to maintain the pH of the solution at a constant value of 8.0 ± 0.1. The resulting precipitate was filtered, washed with distilled water, and dried overnight at 383 K followed by calcination at 773 K for 5 h. A series of AAB supports with various Al/B molar ratios could be obtained by altering the relative amount of aluminum nitrate and boric acid. Some of the physical properties of $Al_2O_3-B_2O_3$ are shown in table 1.

Catalyst preparation. Catalysts containing various amounts of rhenium were prepared by an incipient wetness impregnation method, using 75.6 wt% aqueous solutions of perrhenic acid (Strem Co.). The supports were AAB with various Al/B molar ratios. After drying in an oven at 110°C for 4 h, the impregnated supports were calcined at 550°C for 4 h and then cooled in air.

Temperature-programmed reduction (TPR). Re/AAB catalyst was set in a U-type quartz reactor tube. The sample (0.2 g) was heated in a nitrogen flow at 120°C for 4 h to desorb water and then cooled to ambient temperature. Then the sample was heated in a H_2/Ar reducing gas mixture ($H_2 = 3$ ml/min, $Ar = 27$ ml/min) from room temperature to 650°C with a heating rate of 10°C/min and retained at 650°C for 1 h. Water formed by reduction or dehydration was trapped in a 4A molecular sieve column. After the gas mixture had passed through the molecular sieves, its composition was monitored contin-

Table 1

The physical properties of $Al_2O_3-B_2O_3$ support

Al/B (molar ratio)	Surface area (m^2/g)	Pore volume (cc/g)	Pore diameter (Å)
2.0	196	0.46	63
3.5	210	0.36	50
5.0	229	0.35	48
8.0	242	0.36	48
12.0	239	0.39	49
20.0	294	0.44	43

uously with a thermal conductivity detector (TCD). The T_{max} was the temperature at which the consumption of hydrogen reached a maximum.

Temperature-programmed desorption (TPD) of NH_3. In a typical experiment 100 mg of calcined sample in a U-shaped quartz tube was activated in dry air at 300°C for 5 h. After cooling to room temperature, high purity ammonia (99.99%) was adsorbed. The temperature was raised and held at 150°C until no physical adsorbed NH_3 was desorbed. The temperature was then raised with a rate of 5°C/min to 700°C under a stream of He at 30 ml/min. Ammonia desorbed from the sample was trapped in a buffer solution of boric acid and autotitrated with sulfamic acid. The T_{max} was the temperature at which the desorbed amount of NH_3 reached a maximum.

Metathesis activity measurement. The activity tests of metathesis reaction were carried out in a stainless steel tube microreactor, equipped with a flow controller and heated by an electrical heater. The metathesis reaction was then studied under the following conditions: temperature 30°C; pressure 760 mmHg; weight hourly space velocity WHSV = 0.82 h^{-1}; catalyst 2.5 g. During each run, products were analyzed at intervals with an on-line GC. The analysis column was a 24 ft × 1/8 in. o.d. stainless steel tube column, packed with 25% Sebaconitrile on Uniport C 80/100 mesh, operated under the following conditions: oven temperature, 40°C; helium flow rate, 20 ml/min.

3. Results and discussion

In order to investigate the effect of support for the reaction of propylene metathesis, three kinds of support, i.e. Al_2O_3, Al_2O_3–P_2O_5 (AAP) and Al_2O_3–B_2O_3 (AAB) were used for the preparation of supported rhenium oxide catalysts. The Al_2O_3 and AAP supports were prepared by the precipitation method as described in our previous papers [16,17]. Fig. 1 shows the catalytic activity and stability of these three catalysts. It indicated that Re_2O_7/AAB gave the highest activity and stability for propylene metathesis.

A series of Re_2O_7/AAB catalysts with various Al/B molar ratios were also studied. The results are shown in fig. 2. The optimum Al/B molar ratios of AAB for the conversion of propylene metathesis were found to be in the range of 4–10. The regenerability of Re_2O_7/AAB catalyst was also investigated. After each activity test run, the used catalyst was purged with air at 550°C for regeneration, and then propylene was charged again for activity test. Fig. 3 shows the change of propylene conversion and ageing rate with the number of regeneration cycle. It indicates that there is no significant change of conversion and ageing rate after 6 regeneration cycles.

Xu and Mol [13] pointed out that the activity of silica–alumina supported rhenium catalysts for metathesis was higher than that of alumina supported ones. The high activity could be ascribed to their high acidity, especially high

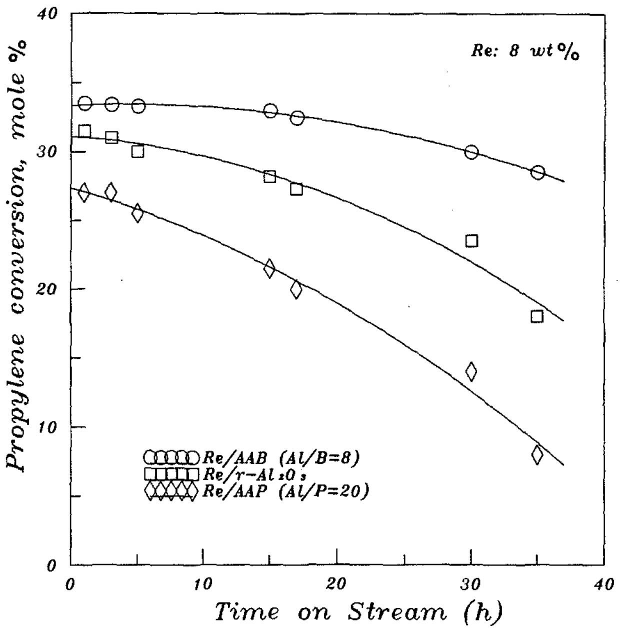

Fig. 1. The change of propylene conversion with time on stream for different kinds of catalysts, Re/AAB (Al/B = 8), Re/Al_2O_3 and Re/AAP (Al/P = 20); reaction conditions: temperature 30°C, pressure 760 mmHg, WHSV = 0.82 h^{-1}.

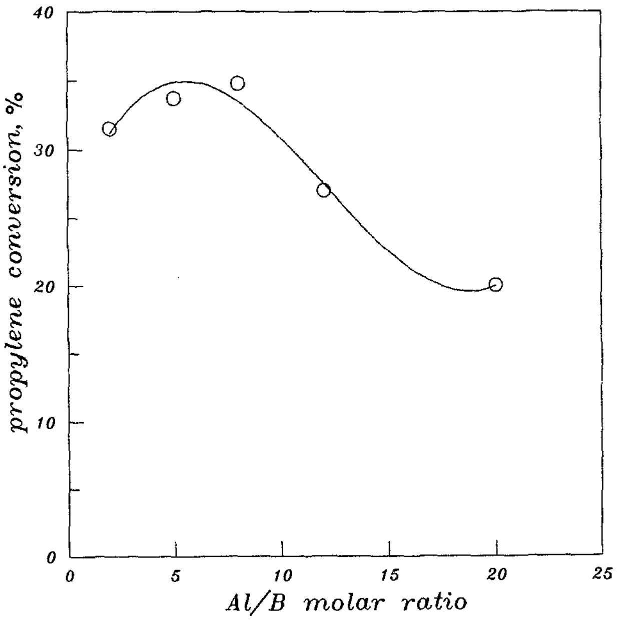

Fig. 2. The conversion of propylene metathesis versus the Al/B molar ratio of the AAB support; reaction conditions are the same as mentioned in fig. 1.

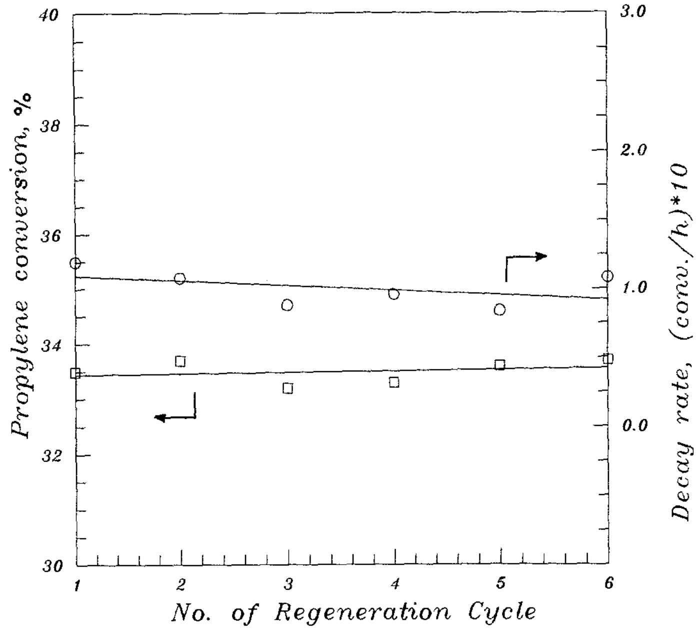

Fig. 3. The change of propylene conversion and ageing rate with the number of regeneration cycle; reaction conditions as in fig. 1.

Brønsted acidity. The stabilizing effect of silica-alumina for rhenium species at intermediate oxidation state might also play a role. Izumi and Shiba [18] also measured the activity of a series of alumina-boria catalysts and they found that the acidity is mainly of Brønsted character.

In this work, we use the NH_3 TPD method to measure the acidity of the catalysts, where the higher T_{max} relates to higher acidity of the catalyst. The T_{max} changes of AAB-supported catalysts with various molar ratios are shown in fig. 4. It indicates that the T_{max} value increases with increasing Al/B molar ratio through a maximum at $Al/B = 4$ and then decreases. It could be concluded that the higher acidity of Al_2O_3 due to the addition of boria was not the only contribution to the higher activity of the Re_2O_7/AAB catalyst.

The TPR technique was used to characterize the catalyst, where the higher T_{max} relates to the higher stability of Re_2O_7. The T_{max} changes of rhenium catalysts with various Al/B molar ratios are shown in fig. 5. An optimum T_{max} value was found to be at $Al/B = 8$. It indicates that the higher resistance to reduction of supported Re_2O_7 due to the addition of boria could be another contribution to the higher activity. Fig. 6 also shows the T_{max} change with the increase of Re_2O_7 content for Al_2O_3 and AAB based catalysts. For all levels of Re_2O_7, the T_{max} of AAB based catalysts are higher than those of Al_2O_3 based catalysts. This could be well correlated to the different activities of Re_2O_7/AAB and Re_2O_7/Al_2O_3 as shown in fig. 1. Spronk et al. [19] also pointed out that the

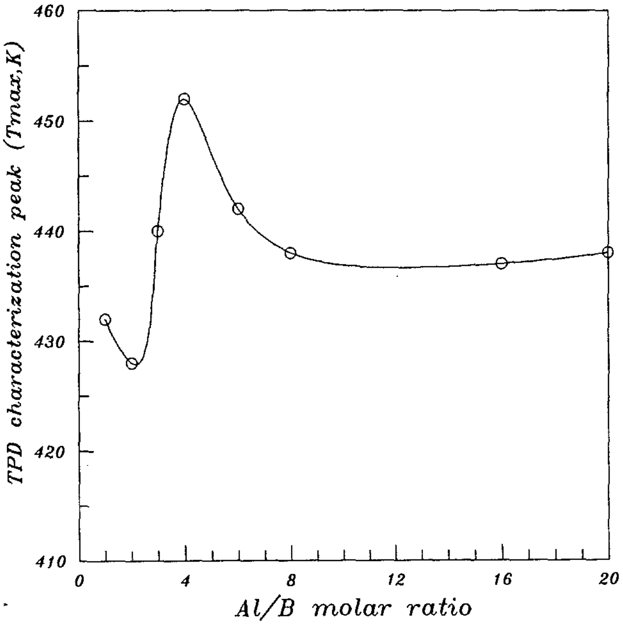

Fig. 4. The T_{max} of NH_3 TPR versus the Al/B molar ratio of AAB support.

influence of the type of support on the relationship between metathesis activity and rhenium oxide loading can be related to the number and that the Brønsted acidity of certain hydroxyl groups is due to the local strong electron withdrawing

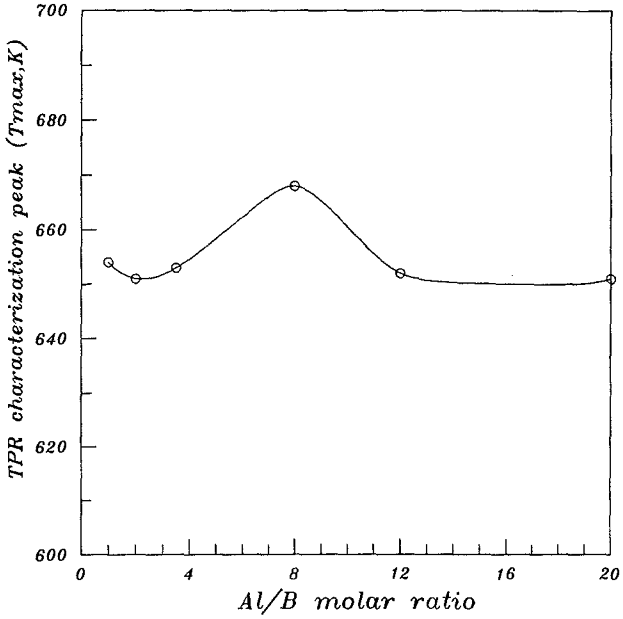

Fig. 5. The T_{max} of TPR versus the Al/B molar ratio of AAB support.

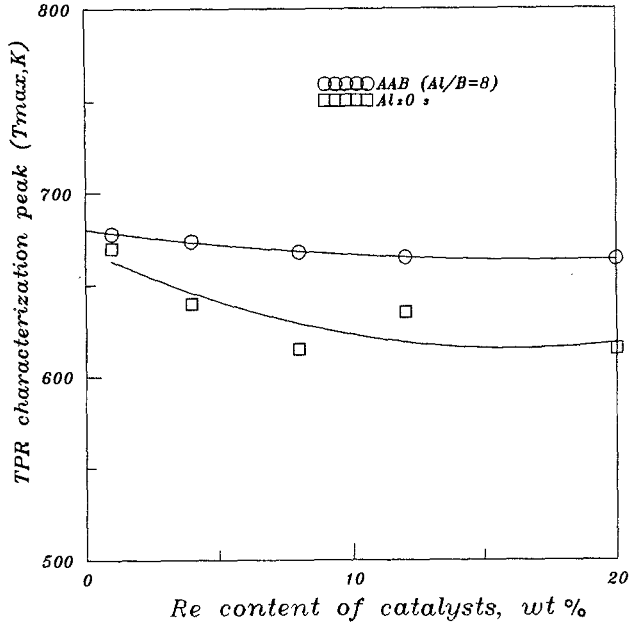

Fig. 6. The T_{max} change of TPR with the increase of Re_2O_7 content for different kinds of catalysts, Re_2O_7/Al_2O_3 and Re_2O_7/AAB.

properties of the support. Therefore, the improvement of metathesis activity of Re_2O_7/Al_2O_3 due to the addition of boria could be attributed to the following factors: it maintains Re at the most favorable oxidation state for the formation of initial metal carbene and increases the acidity of the Al_2O_3 support.

4. Conclusions

From the above results and discussions, we conclude the following:

(1) For propylene metathesis, the Re_2O_7/AAB catalyst is more active, stable and regenerable than the conventional Re_2O_7/Al_2O_3 catalyst.

(2) Boron promotes the activity of Re_2O_7/AAB by maintaining Re at a desirable oxidation state and increasing support acidity.

(3) The optimum Al/B molar ratios are in the range of 4–10.

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