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Rhenium oxide supported on mesoporous organized alumina as a catalyst for metathesis of 1-alkenes

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New type of heterogeneous catalyst for metathesis of linear 1-olefins based on rhenium (VII) oxide supported on organized mesoporous alumina was developed. This catalyst operates under very mild reaction conditions without any solvent and the highest activity was achieved at the reaction temperature of 60 °C with selectivity to symmetrical olefin over 90%. The optimum loading of rhenium (VII) oxide was found to be between 9 and 15 wt% of Re. The initial activity was dependent on pore size diameter—the larger pore diameter, the higher initial catalytic activity under the same reaction conditions.

KEY WORDS: organised mesoporous alumina; rhenium oxide; 1-alkene metathesis.

1. Introduction

The availability and easy preparation of raw materials and petrochemical intermediates represent an important issue of up-to-date chemical industry. In this respect, any new reaction or even technological process is welcome, which is also connected with the development of new types of heterogeneous catalysts, in particular, operating in continuous processes. Metathesis of olefins represents one example of industrially very important reaction, which is used for transformation of less desired to more desired materials with a large variety of possible applications. The applications include self-metathesis, cross-metathesis, ring closing and ring opening metathesis or metathetic polymerizations giving significant number of products of interest [1,2].

The first commercial application of metathesis dates back to 1966 when Triolefin Process was put into operation, in which propylene was transformed into a mixture of ethylene and 2-butene. Later on the reverse process leading to the formation of propylene has been developed based on the global market requirements for propylene [3]. Other metathesis processes are now under operation by BASF, IFP, Shell and others and recently even the production of several pheromones based on metathesis reactions was announced [2].

Modern homogeneous metathesis catalysts are stable carbene complexes of Ru, Mo and W [4–6]; however, there exist a number of heterogeneous catalysts based on Re_2O_7/Al_2O_3, MoO_3/SiO_2 or WO_3/SiO_2, which can operate either as such or addition of cocatalysts (e.g., tetraalkyltin) is required [3]. Among them Re_2O_7/Al_2O_3 attracts a special attention because of its activity at mild conditions and tolerance to functional groups of substrate. The supporting or immobilization of active transition-oxide metal species on proper inorganic support represents a key step in the synthesis of highly active and selective catalysts and therefore, the effect of chemical composition and textural properties of inorganic support are widely studied [7]. New era of preparation of heterogeneous catalysts started with the first successful synthesis of mesoporous molecular sieves based on siliceous [8] or alumina materials [9]. These mesoporous molecular sieves exhibit high surface areas even above 1000 m^2/g, large void volumes and narrow pore size distribution in the mesoporous range. They were applied as supports for transition metal oxides, e.g., in systems MoO_3 over mesoporous alumina for hydrodesulfurization of thiophene or MoO_3 over hexagonal mesoporous silica for olefin metathesis [10,11]. Up-to-now only short communication lacking appropriate experimental details on the utilization of Re(VII) oxide on mesoporous alumina was published [12].

In this contribution we report on the synthesis of the new type of metathesis heterogeneous catalyst for metathesis of linear 1-alkenes based on rhenium oxide supported on organized mesoporous alumina by thermal spreading method. The effect of reaction conditions, metal oxide loading and pore size diameter on the activity and selectivity in metathesis reactions is described in a detail.

2. Experimental

2.1. Materials

Sample of organised mesoporous alumina (OMA-3) was prepared from $Al(O\text{-sec. }Bu)_3$ in acetonitrile at

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laboratory temperature using lauric acid as a structure-directing agent according to the procedure given elsewhere (number in OMA label corresponds with the pore diametre of the sample) [13]. The samples OMA-5 and OMA-6 were synthesized using Pluronic PE 9400 and 10400 (BASF). After the synthesis, the individual samples were washed in ethanol, filtered, dried at laboratory temperature and calcined at 450 °C (OMA-3) and 550 °C (OMA-5, OMA-6) to remove structure directing agents. Sample of OMA-7 was kindly provided by J. Peréz-Pariente (Institute of Catalysis and Petrochemistry, Madrid, Spain). For comparison, a sample of conventional alumina (ALCOA) was used (having surface area of 340 m^2/g). NH_4ReO_4 (Fluka, puriss.) was used as obtained. 1-Octene (Fluka, >97%), 1-decene (Spolana, purum,) and 1-Octadecene (Fluka, purum) were purified by passing through activated alumina and dried with sodium.

2.2. Catalyst preparation and characterization

Thermal spreading method was used for rhenium oxide deposition on alumina support, which is based on grinding of OMA and/or ALCOA with calculated amount of NH_4ReO_4 at room temperature and then calcined at 550 °C for 6 h. Using this approach, catalysts Re/OMA-3, Re/OMA-5, Re/OMA-6, Re/OMA-7 and Re/ALCOA were prepared. Before use, the catalysts were activated by heating at 500 °C for 3 h in air. XRD (Siemens D5005 with Cu Kα) and adsorption isotherms of nitrogen (Micrometrics ASAP 2010 instrument) were used to characterise the structural and textural properties of alumina support and catalyst prepared. The concentration of Re in individual catalysts was determined by ICP AES (Ecochem Co., Prague, Czech Republic).

2.3. Catalyst activity

Catalytic experiments were carried out in a batch reactor equipped with magnetic stirrer (50 rpm) under argon atmosphere at temperatures 25, 40 and 60 °C. In a typical experiment, 50 mg of catalyst was placed into a glass reactor (10 mL) and then heated in an argon flow at 500 °C (for 20 min). After cooling down to the preset reaction temperature, 8 mmol of substrate was added. During the reaction, 30 μL of reaction mixture was sampled for GC-analysis in a given time intervals. High-resolution gas chromatograph Agilent 6890 with DB-5 column (length: 50 m; inner diameter: 320 μm; stationary phase thickness: 1 μm) was used for product analysis, while a GC-MS (HP 5890 + 5971A) for identification of individual reaction products. Total conversion of 1-alkene (K) and selectivity related to the self-metathesis products (S) were calculated based on the material balance using following formulas: $K = 2(n_p + \Sigma n_i)/(n_s + 2n_p + 2\Sigma n_i)$, $S = n_p/(n_p + \Sigma n_i)$, where n_S, n_P, n_i are the molar amounts of starting alkene (including its isomers), self-metathesis product and cross-metathesis products higher than starting alkene, respectively.

3. Results and discussion

Both mesoporous aluminas and Re/OMA catalysts prepared were characterised by X-ray powder diffraction at low-angle degrees (not shown here) and nitrogen adsorption isotherms. Figure 1A provides the adsorption isotherms of OMA-3 and OMA-5 while in figure 1B the adsorption isotherms of parent OMA6 and those after modification with 9.5 and 12.0 wt% of Re are given. All three nitrogen isotherms of parent OMA-3, OMA-5 and OMA-6 exhibit steep increase in the adsorbed amount of nitrogen around $p/p_o = 0.4$, 0.6 and 0.7, respectively, indicating increasing pore size diameter and narrow pore size distribution. In contrast, commercial ALCOA alumina and Re/ALCOA with 12 wt% of Re are characterised by a very broad pore-size distribution (figure 2) including a considerable amount of micropores. All Re-alumina catalysts showed the decrease in the surface areas and void volumes caused by addition of Re oxide, however, for Re/OMAs no significant change of the pore-size diameter was observed. For ALCOA, the decrease in surface area is much larger compared to OMAs modified by the same amount of Re, probably due to the blocking of significant part of micropores by Re oxide species (volume of micropores before modification = 0.097 cm^3/g, volume of micropores after modification = 0.026 cm^3/g).

X-ray powder diffraction data of Re/OMA-6 catalyst showed the disappearance of crystalline phase during the thermal treatment (figure 3). It is inferred that Re oxide in the form close to the monolayer is present. Re content determined by ICP AES was in a good agreement with Re loading calculated from amount of NH_4ReO_4 used for alumina impregnation, i.e, no Re lost during calcination was observed (contradictory to the observation by Hardcastle et al. [14] that for high

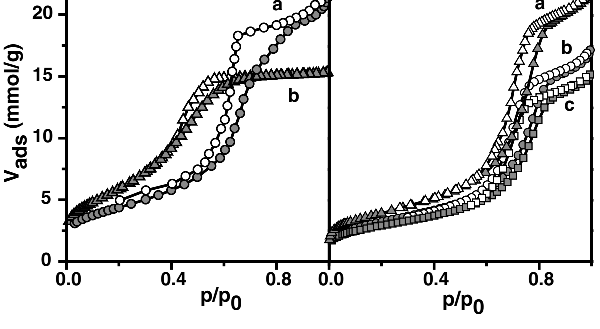

Figure 1. Nitrogen adsorption isotherms of OMA-3 (a) and OMA-5 (b) (A) and OMA-6 (a), Re/OMA-6 with 9.5 (b) and 12.0 (c) wt% of Re (B).

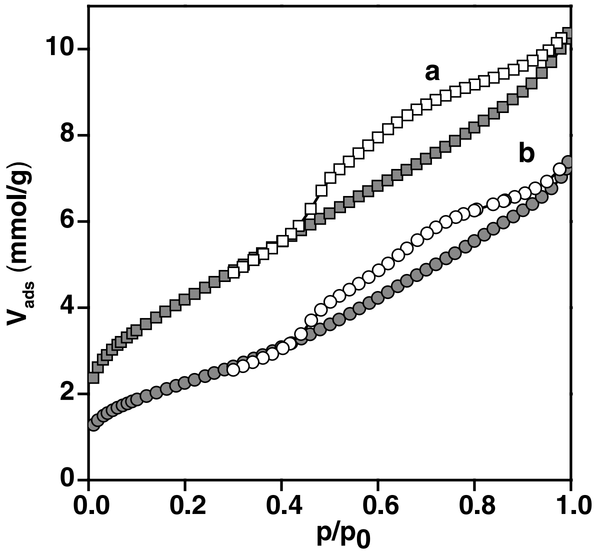

Figure 2. Nitrogen adsorption isotherms of commercial alumina ALCOA (a) and that one modified with 12.0 wt.% of Re (b).

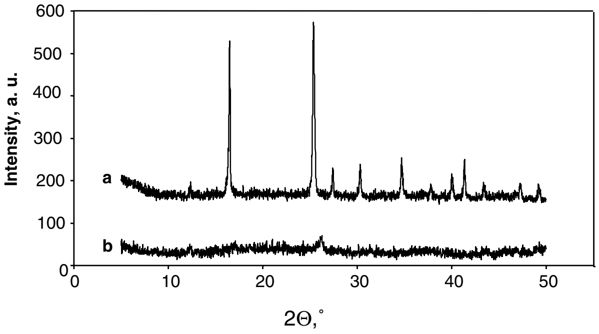

Figure 3. XRD crystalographic data (a) for the mixture of NH_4ReO_4 and OMA-6 (15 wt% of Re) and (b) for Re/OMA-6 (loading 15 wt% of Re).

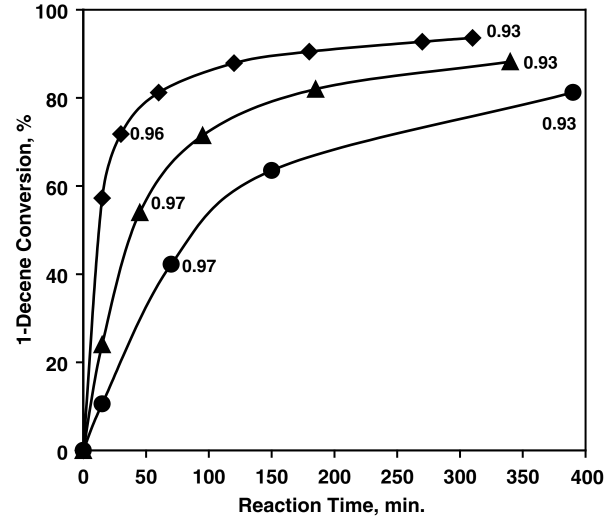

Figure 4. 1-Decene conversion *vs.* time curves for Re/OMA-6 catalyst at 25 °C (●), 40°C (▲) and 60°C (◆). Catalyst loading = 9.5 wt% of Re, numbers at experimental points give the reached selectivity.

loading samples actual Re concentration was significantly lower than that calculated from initial amount of NH_4ReO_4).

Metathesis of 1-alkenes proceeds according to the following equation:

$$2CH_3(CH_2)_nCH = CH_2 \leftrightarrow CH_2 = Ch_2 + CH_3(CH_2)_n \times CH = CH(CH_2)_nCH_3.$$

In principal, reaction equilibrium is reached at 50% conversion, however, removing ethylene from the reaction mixture, the equilibrium can be considerably shifted towards the reaction products. The time dependence of 1-decene conversion during metathesis reaction with Re/OMA-6 catalyst at 25, 40 and 60 °C is given in figure 4. It is seen that Re/OMA-6 catalyst exhibited high activity and selectivity at these temperatures. In addition to the main product, 9-octadecene, only small amount of alkenes with shorter chains originating from double bond shift isomerization of starting 1-decene and subsequent cross-metathesis was observed. No dimers and/or oligomers were found. Selectivity slightly decreased with increasing conversion as a result of slow 1-decene isomerization reaction. No influence of reaction temperature on the selectivity to 9-octadecene was found.

The influence of Re loading on activity and selectivity of Re/OMA-5 catalyst in 1-decene metathesis is depicted in figure 5. It is seen that catalyst activity increased steeply with increasing Re content in low loading region, but in the region from 9.5 to 15 wt% the activity changes are nearly negligible. Similar activity dependence on the loading was also observed for Re/OMA-6 in 1-octene metathesis. This finding corresponds to the

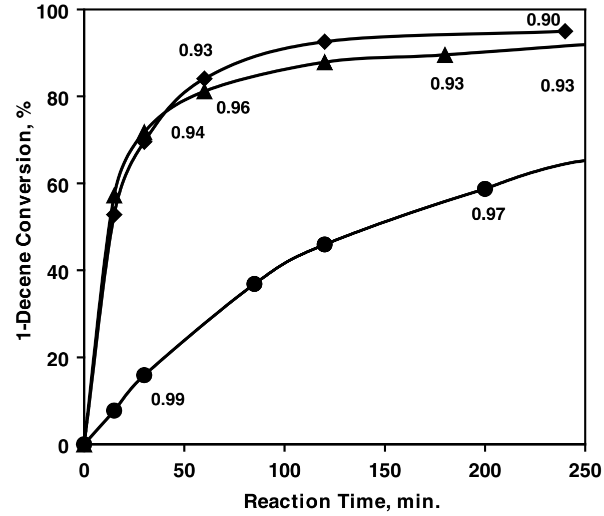

Figure 5. 1-Decene conversion *vs.* time curves for Re/OMA-6 catalyst with 4.5 wt% of Re (●), 9.5 wt% of Re (▲) and 15 wt% of Re (◆). Reaction temperature 60°C, numbers at experimental points give the reached selectivity, for 4.5 wt% of Re conversion 89% and selectivity 0.95 were reached at reaction time 23 h.

results given in ref. [12] but seems to be in contradiction to the loading-dependence activity for Re_2O_7 on conventional alumina reported earlier [15]. For Re_2O_7/Al_2O_3 catalyst the initial rate of propene metathesis was found to increase with increasing Re content up to 18 wt% of Re_2O_7. It is known that the active phase in rhenium oxide catalyst consists of ReO_4 groups attached to the surface by covalent Al–O–Re bond [14,16]. It is believed that 18 wt% of Re_2O_7 represent the limit of the surface monolayer capacity for these groups [15,17] (about 3 ReO_4 groups/nm^2). For Re/OMA-5 loaded with 9.5 wt% of Re, the calculation gives only 0.9 Re group/nm^2, i.e., rather low under these capacity limit. However, the number of catalytically active species is expected to be very low (< 1% of Re amount on catalyst surface was found for Re_2O_7/Al_2O_3 catalyst [15,18]) and may not be proportional to the total amount of Re on the surface. The process of creation and stabilization of active sites on alumina surface is not yet clear, but it is assumed that electronic and/or steric influence of close surrounding of individual Re groups is decisive for the formation of active Re-species. Therefore, the Re groups located only in special positions give rise to the active species and character and concentration of these special positions may vary with type of alumina support. In this respect, the optimum catalyst loading is more probably connected with limited concentration of these special positions than with surface monolayer capacity. Selectivity dependence on the catalyst loading is nearly negligible for both 1-decene and 1-octene metathesis. For final conversion only very slight decrease from $S = 0.95$ (4.5 wt% loading) to $S = 0.90$ (15 wt% loading) was found, which may indicate an increasing rate of isomerization with increasing Re loading.

In figure 6 conversion curves of 1-decene metathesis catalysed with three mesoporous alumina catalyst of different pore size (Re/OMA-3, Re/OMA-5, Re/OMA-7) possessing the same amount of Re (12 wt%) and with conventional alumina supported catalyst Re/ALCOA of the same loading are compared. With all Re/OMA catalyst the metathesis of 1-decene proceeds very fast in comparison with Re/ALCOA, e.g. (i) after 30 min from initiation, 1-decene conversion of 58% was reached with Re/OMA-3, i.e about 10 times higher than that reached with Re/ALCOA at this time, (ii) after 120 min reaction, conversion of more than 80 % was reached with all Re/OMA catalyst, but not more than 55 % was reached with Re/ALCOA even after 23 h. On the other hand, the selectivities at final conversions were always above 0.9. Even higher difference in activity between Re/OMA catalysts and Re/ALCOA was observed for metathesis of 1-octene at 40 °C: 1-octene conversion of 47% at 30 min of reaction with Re/OMA-5 (12 wt% of Re) in comparison with the conversion of about 1% with Re/ALCOA of the same loading at the same time. These differences clearly show the superiority of Re/OMA catalysts to the catalyst using conventional alumina as a support. The reason for this superiority is not completely understood. At least two factors may be taken into account: (i) for Re/ALCOA catalyst, a considerable fraction of total Re may be accumulated in micropores where it is not accessible for substrate molecules (it is seen from a dramatic decrease in micropore volume after modification with Re), (ii) for Re/OMA catalyst, the amount of positions suitable for stabilizing catalytically active Re-species may be higher than for Re/ALCOA. As establishing detailed structure of Re site responsible for the highest activity is a difficult task due to their low amount and there are no specific reasons for substantial differences in surface properties of OMA and of ALCOA, we believe that the presence of micropores in conventional alumina is the decisive factor limiting the metathesis activity of Re/ALCOA in comparison with Re/OMA catalysts. On the other hand, the detail investigation of the OMA surface, which is now in the beginning, may throw a new light on this field.

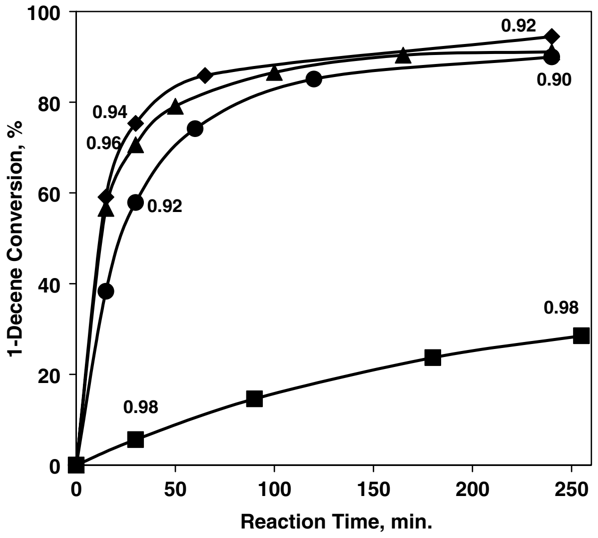

Figure 6. 1-Decene conversion *vs.* time curves for Re/OMA-3 (●), Re/OMA-5 (▲), Re/OMA-7 (◆) and Re/ALCOA (■). Catalyst loading = 12 wt% of Re, reaction temperature = 60°C, numbers at experimental points give the reached selectivity, for Re/ALCOA conversion 55% and selectivity 0.93 were reached at reaction time 23 h.

The influence of catalyst pore size on catalytic activity of individual Re/OMA catalysts is also seen from figure 6. At early stage (after 15 and 30 min of the reaction), 1-decene conversion increased in the order Re/OMA-3 < Re/OMA-5 < Re/OMA-7, i.e., in the order of the increasing pore size. It may reflect the influence of different pore size on accessibility of active sites for 1-decene molecules and on products release from the catalyst pores at early stages of the reaction, while for longer periods of the reaction some adsorption–desorption equilibrium is formed resulting in the same conversions after 1 h of reaction.

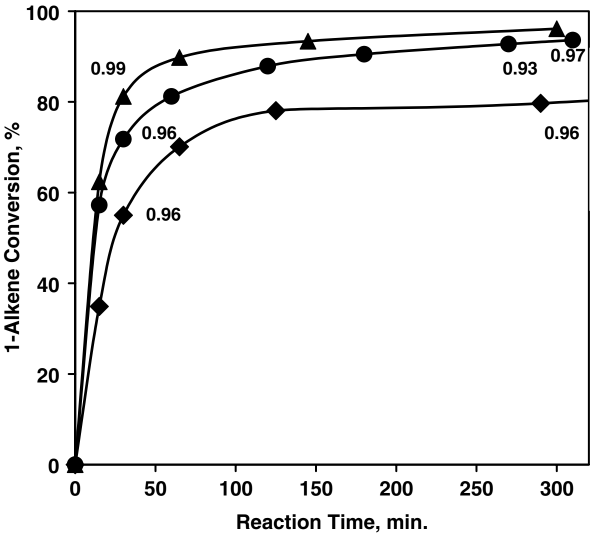

Figure 7. Conversion *vs.* time curves for metathesis of 1-octene (▲), 1-decene (●) and 1-octadecene (◆). Catalyst Re/OMA-6, loading 9.5 wt%, reaction temperature 60°C, numbers at experimental points give the reached selectivity.

Figure 7 shows conversion curves for metathesis of neat 1-octene, 1-decene and 1-octadecene with Re/OMA-6 at 60 °C. It is seen that Re/OMA-6 exhibited high activity and selectivity regardless of the substrate. The initial rate decreased in the order 1-octene > 1-decene > 1-octadecene. Based on the conversions after 15 min of the reaction, the relative initial reaction rates for 1-octene, 1-decene and 1-octadecene are 1:0.9:0.6. The decrease in the reactivity of 1-alkenes with increasing chain length was described before [19,20] and was attributed to the increasing ratio of degenerate metathesis to productive metathesis and/or to the decreasing rate of product desorption with increasing chain length of substrate. In the literature, relative activities in alkene homologue series from C_6 to C_{10} were reported to decrease by an average factor of about 0.15 [20] or even of 0.22 [19] per C atom, i.e., more rapidly than we have found for Re/OMA-6. A higher efficiency of Re/OMA catalysts compared to that prepared with conventional alumina support may be inferred from these findings.

Table 1
Texture characteristics of supports and catalyst used

Sample	S_{BET} (m^2/g)	V (cm^3/g)	D (nm)
OMA-3	400	0.632	3.5
OMA-5	350	0.795	5.5
OMA-6	314	0.745	6.5
OMA-7	300	0.850	7.0
ALCOA	342	0.355[a]	–
Re/ALCOA	186	0.250[a]	–
Re/OMA-6[b]	257	0.584	6.8
Re/OMA-6[c]	232	0.527	7.0

[a] Total volume of pores (including micropores).
[b] 9.5 wt.% of Re.
[c] 12.0 wt.% of Re.
S_{BET}: BET surface area; V: mesopore volume, D: average pore diameter.

4. Conclusions

New heterogeneous catalyst for metathesis of higher 1-alkenes was prepared by thermal spreading of ammonium perrhenate on organised mesoporous alumina. This catalyst operates at mild conditions and without any solvent exhibiting high activity and more than 90% selectivity to the key product (higher symmetric internal alkene). The activity of OMA based catalyst was found to be about 1 order of magnitude higher in comparison with that of Re catalyst of the same loading but using conventional alumina support. Optimal loading for OMA based catalysts was found to lie in the region from 9 and 15 wt% of Re. With increasing pore diameter in the region from 3.5 to 7.0 nm, the initial reaction rate of metathesis increased significantly.

Acknowledgments

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