

The application of metal oxide vapour synthesis to the preparation of molybdena catalysts: The isomerization of 1-hexene

Mark A. Keane¹, Elmer C. Alyea^{*}

Department of Chemistry & Biochemistry, University of Guelph, Guelph, Ont. N1G 2W1, Canada

Received 10 July 1995; accepted 27 September 1995

Abstract

A novel molybdena catalyst has been prepared by metal oxide vapour synthesis (MOVS) and used to promote the vapour phase isomerization of 1-hexene to the two stereoisomeric forms of 2-hexene. Reproducible diffusion-free isomerization rates are reported and compared to those achieved using a commercial sample. Activity and product composition are plotted as a function of time-on-stream and reaction temperature. The degree of isomerization drops markedly over the first one to two hours and this is attributed to an occlusion of the active sites by carbonaceous deposits. The reaction is zero order with respect to 1-hexene concentration and identical rates are achieved using a helium or nitrogen carrier gas. The MOVS system delivers appreciably higher reaction rates compared with the commercial catalyst and apparent activation energy values of 40 and 30 kJ mol⁻¹ are recorded for the commercial and laboratory prepared catalysts, respectively. The observed isomeric yields result from the direct conversion of 1-hexene where a surface promoted interconversion of isomers can be discounted and the ultimate stereospecificities are ascribed to steric effects.

Keywords: Metal oxide; Vapour; Synthesis; Molybdena; Isomerization; Hexene

1. Introduction

Molybdena catalysts, where the term denotes a composite catalyst consisting of molybdenum oxide supported on an activated carrier, are among the most versatile heterogeneous catalytic agents in use today due to the wide range of coordination numbers and oxidation states that they possess. Molybdena–alumina systems alone have been successfully used to promote

hydrogenolysis, isomerization, ring reduction, olefin metathesis, polymerization, dehydrogenation, dehydrocyclization and dehydrocondensation reactions [1] where catalyst preparation has normally utilized impregnation methodologies [2]. Metal oxide vapour synthesis (MOVS) has been established in this laboratory as a method for preparing novel catalytic materials [3,4] that have proved more efficient than conventional catalysts in the partial oxidation of methanol [5] and ethanol [6] and syn gas conversion to alcohols [7]. A similar improvement in the rate of isomerization of 1-hexene is demonstrated in this paper. The conversion of 1-hexene to the two isomeric forms of 2-hexene has been re-

^{*} Corresponding author.

¹ Present address: Department of Chemical Engineering, The University of Leeds, Leeds LS2 9JT, UK.

ported using protonated zeolites [8–10] and platinum [11], cobalt [12] and osmium [13,14] based catalysts but the authors failed to unearth any data relating to the application of molybdena–alumina catalysts to this process. Reproducible isomerization rate data for a $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst prepared by MOVS are reported herein and compared to those generated using a commercial catalyst. The effects of time, temperature and transport limitations on the MOVS catalytic system are considered, the kinetics and stereospecificity of the reaction are presented and the nature of the active sites is addressed.

2. Experimental

2.1. Catalyst preparation and activation

Molybdenum trioxide (Aesar/Johnson Matthey, 99.95%) vaporization was achieved by resistive heating at a pressure of $3 \cdot 10^{-6}$ Torr and the oxide vapours were cocondensed at 77 K with a 250 fold molar excess of anhydrous methanol (Aldrich, 99.9 + %) using the Torrovap apparatus that is described in full detail elsewhere [3]. The cocondensate was allowed to slowly come to room temperature and formed a clear colourless solution which was removed from the reaction flask via a cooled Schlenk tube. The γ -alumina (Aesar/Johnson Matthey, 99.99%, $188 \text{ m}^2 \text{ g}^{-1}$) support was then introduced to the cocondensate and the combined mixture was stirred for 36 h to ensure an even deposition throughout the sample, at which point the solution volume was reduced by vacuum evaporation to recover a white solid, the supported catalyst precursor. Alternatively, the cocondensate was left to stand at room temperature and a white sheet-like precipitate formed which was recovered and may be denoted as the unsupported precursor. Both the supported and unsupported catalyst precursors were lightly ground, dried at 383 K and exposed to UV radiation ($\lambda = 350 \text{ nm}$) for seven days. The samples were further activated by calcination in

a $120 \text{ cm}^3 \text{ min}^{-1}$ stream of dry air at a rate of 10 K min^{-1} to a final temperature of 673 K which was maintained for 18 h prior to catalysis. A sample of a commercial 10% MoO_3 on γ -alumina (Aesar/Johnson Matthey) catalyst was likewise calcined for comparative purposes.

2.2. Catalytic procedure

All the catalytic reactions were carried out under atmospheric pressure in a fixed bed glass reactor (i.d. = 15 mm) over the temperature range $373 \text{ K} \leq T \leq 573 \text{ K}$. The catalyst was supported on a glass frit and a layer of glass beads above the catalyst bed ensured that the hydrocarbon reached the reaction temperature before contacting the catalyst. The reactor temperature was monitored by a thermocouple inserted in a thermowell within the catalyst bed where the reactor temperature was constant to within $\pm 1 \text{ K}$. A Sage pump (model 341 B) was used to deliver the 1-hexene feed via a syringe at a fixed rate which had been carefully calibrated; the partial pressure of 1-hexene was in the range 20–64 Torr. The hydrocarbon vapour was carried through the catalyst bed in a stream of purified helium or nitrogen, the flow rate of which was set using Brooks mass flow controllers. Rate measurements were made using catalyst samples sieved in the 125–150 μm mesh range, at a space velocity of 1543 h^{-1} (STP) and $W/F < 100 \text{ g mol}^{-1} \text{ h}$ where W is the weight of activated catalyst and F is the flow rate of 1-hexene. Pseudo-steady state differential conversions were kept below 20% by varying W in order to avoid heat and mass transfer effects. The possible contribution of external and internal reactant/product diffusion to the overall reaction rate was monitored by (a) varying W/F value in the overall range 17–127 $\text{g mol}^{-1} \text{ h}$ by altering both parameters and (b) using three separate batches of catalyst with particle diameters in the overall range 50–300 μm . The reactor effluent was frozen in a dry ice/acetone trap for subsequent analysis. Product analysis was made using a Varian 3400 GC

chromatograph equipped with a flame ionization detector and employing a 30% Silicone SF96 on 60/80 mesh acid washed Chromosorb W (6 ft. \times 1/8 in.) stainless steel column; data acquisition and analysis was performed using the GC Star Workstation. The overall level of isomerization was converted to mol % isomerization using a 30 point calibration plot. Catalyst regeneration was achieved by heating in a 120 cm³ min⁻¹ flow of dry air at 673 K for 16 h. The 1-hexene (Aldrich, 99 + %) reactant was thoroughly degassed by purging with purified helium followed by a series of freeze/pump/thaw cycles and was stored over activated molecular sieve type 5A.

3. Results and discussion

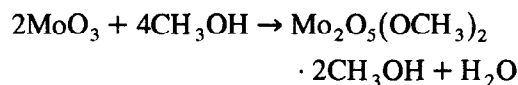
The pertinent physical characteristics of the photoactivated unsupported and supported MOVS catalysts are given in Table 1. The

Table 1

Physical characteristics of the photoactivated unsupported and supported MOVS and commercial molybdena systems

<i>Unsupported catalyst</i>	
surface area	25 m ² g ⁻¹
pore radii	0.8–6.2 nm
particle size	15–50 nm
<i>Supported catalyst</i>	
% MoO ₃ w/w	10
surface area	77 m ² g ⁻¹
pore radii	0.8–1.8 nm
<i>Commercial catalyst</i>	
% MoO ₃ w/w	10
surface area	64 m ² g ⁻¹

evaporation/cocondensation reaction can be simply expressed as



Photoactivation produced formaldehyde and methanol as byproducts and the unsupported calcined catalyst was shown by XRD to contain

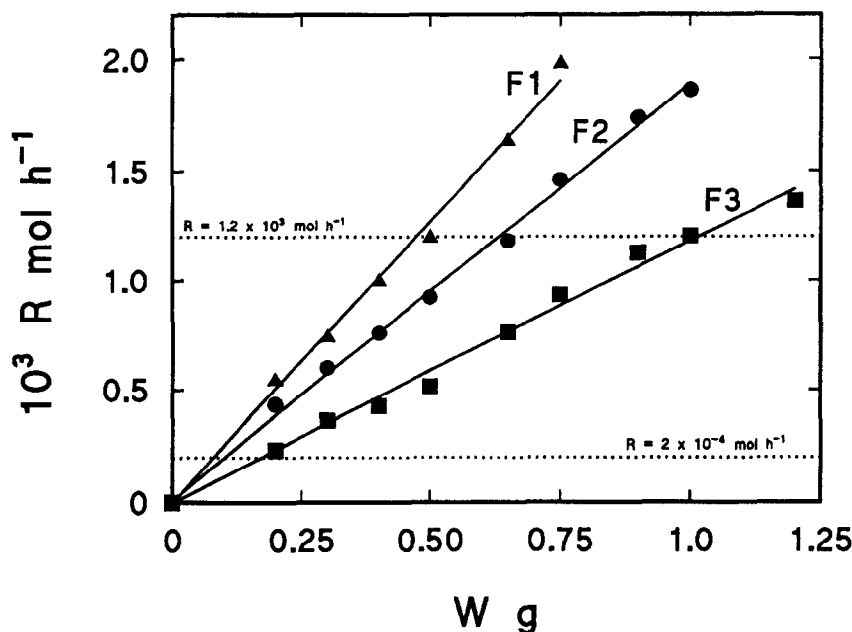


Fig. 1. The relationship between the rate of isomerization at 473 K and the weight of MoO₃/Al₂O₃ (MOVS) for three 1-hexene feed rates: \blacktriangle , F1 = $5.9 \cdot 10^{-3}$ mol h⁻¹; \bullet , F2 = $8.0 \cdot 10^{-3}$ mol h⁻¹; \blacksquare , F3 = $1.2 \cdot 10^{-2}$ mol h⁻¹.

α - MoO_3 and an amorphous component [3]. The supported MOVS system exhibited no apparent crystallinity and the approximate d -spacings agree with those recorded for the unsupported material [15]. The activated unsupported MOVS catalyst is quite distinct from commercial MoO_3 which is typically characterized by a larger particle size (1–15 μm) and a smaller surface area (1–2 $\text{m}^2 \text{g}^{-1}$) [5]. Supporting the MOVS material on the alumina carrier increased surface area and narrowed the pore radius range. In addition, the γ - Al_2O_3 supported MOVS sample is characterized by a higher surface area than that (64 $\text{m}^2 \text{g}^{-1}$) quoted for the commercial catalyst which has the same metal oxide loading.

The isomerization of 1-hexene over the molybdena catalysts yielded the *cis* and *trans* forms of 2-hexene as the only detected products. The activity data presented in this paper were reproducible to better than $\pm 8\%$ and represent the average of at least five separate test samples. The γ - Al_2O_3 carrier exhibits negligible activity for this reaction [11]. The experimental conditions were chosen so that the reaction rate was not influenced by external or internal diffusion. The possible contribution of external diffusion was monitored by independently varying W and F and establishing that the measured rate was constant at a constant value of W/F . A representative case is illustrated in Fig. 1 where isomerization rates of $2.0 \cdot 10^{-4}$ and $1.2 \cdot 10^{-3} \text{ mol h}^{-1}$ obtained using three 1-hexene feed rates correspond to W/F values of 14 ± 1 and $81 \pm 3 \text{ g mol}^{-1} \text{ h}$, respectively. The reactor can be considered to operate with negligible external diffusion retardation within these W/F values and all the rate data were collected at $W/F < 100 \text{ g mol}^{-1} \text{ h}$. In a separate set of experiments the role of intraparticle diffusion was probed by varying the catalyst particle size, in the mesh ranges 50–125, 125–150 and 150–300 μm while maintaining W/F constant. The degree of isomerization was reproducible within experimental error and rate inhibition due to intraparticle

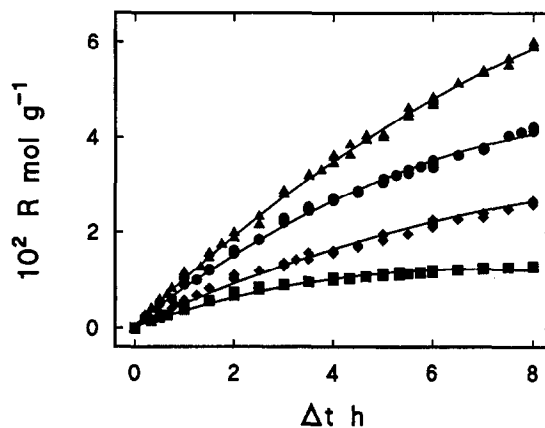


Fig. 2. The variation of isomerization rate over $\text{MoO}_3/\text{Al}_2\text{O}_3$ (MOVS) with time-on-stream at 413 K (■), 473 K (◆), 523 K (●) and 573 K (▲) where the solid lines represent second order polynomial fits.

transport may be discounted over the cited range of particle sizes; the intermediate 125–150 μm mesh range was chosen for the subsequent measurements.

The variation of isomerization rate with time-on-stream is illustrated in Fig. 2 where the reaction rate may be observed to increase with increasing temperature at every time interval. All the activity profiles are characterized by an initial rapid increase in the number of moles of 1-hexene that were converted followed by a gradual reduction in the turnover of reactant which is manifest in a flattening of the curves. Each set of experimentally determined rates can be represented by second order polynomial fits (correlation coefficient > 0.995) which are included in Fig. 2. The degree of isomerization with time of the total concentration of 1-hexene fed to the catalyst over that particular interval is shown in Fig. 3. A rapid drop in percentage conversion is evident, particularly over the first hour on stream and this is followed by the gradual attainment of a constant level of isomerization of the introduced reactant. Prolonged use of the catalyst is however accompanied by a gradual deactivation which ultimately renders the system inactive. The catalyst can be reactivated by heating in air at 673 K to generate near identical time-on-stream profiles and the rate

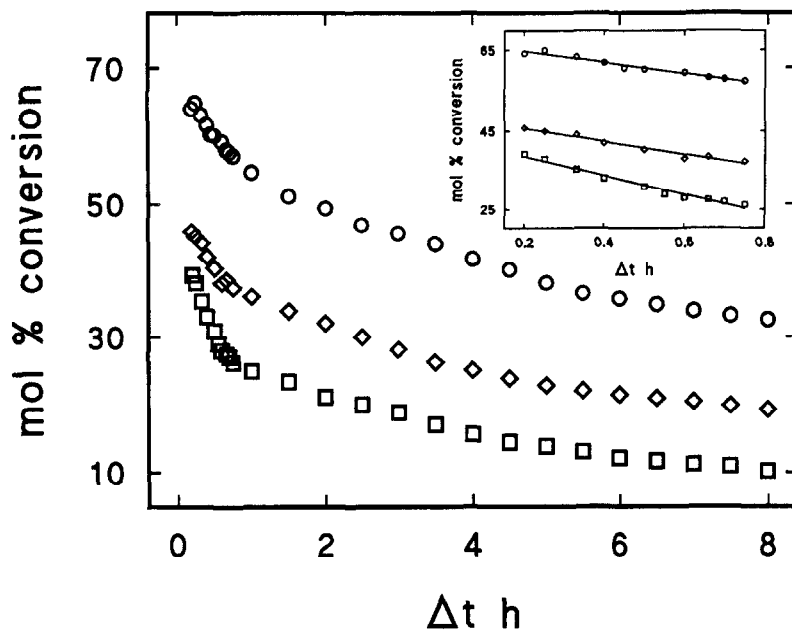


Fig. 3. The effect of time on the degree of isomerization of the 1-hexene feed over $\text{MoO}_3/\text{Al}_2\text{O}_3$ (MOVS) at 413 K (\square), 473 K (\diamond) and 523 K (\circ); Inset: linear relationship between conversion and time over the first hour on stream, symbols as above.

data presented in Fig. 2 is generated from a series of catalytic runs. A similar loss of activity was reported for the conversion of 1-butene in a microcatalytic pulse system where conversion decreased with pulse number as polymeric material formed on the catalyst [16]. The initial marked drop in activity observed for the continuous flow system used in this study may also be due to the occlusion of active sites by carbon deposition. The surface formation of such deposits appears to be time consuming and a sufficient proportion of the active species remains unpoisoned to promote isomerization and achieve a near steady state conversion after four to eight hours on stream. It is instructive to note that the initial loss of activity is proportionally greater at the lower reaction temperature. The drop in mol% conversion over the first hour on stream is better illustrated in the inset to Fig. 3 where the rate of deactivation over $\Delta t = 0.20$ – 0.75 h at 413 K was 1.7 times more than that recorded at 523 K. At the higher temperature the turnover of 1-hexene on the surface was

greater and rate inhibition by irreversibly adsorbed material was accordingly reduced.

The near steady state conversion of 1-hexene is directly proportional to the catalyst weight/feed concentration quotient as illus-

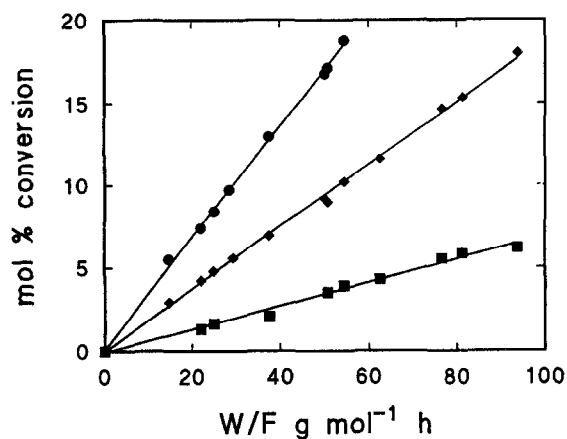


Fig. 4. Linear dependence of conversion on W/F for the isomerization of 1-hexene over $\text{MoO}_3/\text{Al}_2\text{O}_3$ (MOVS) at 413 K (\blacksquare), 473 K (\blacklozenge) and 523 K (\bullet) revealing a zero order dependence of rate on hydrocarbon concentration.

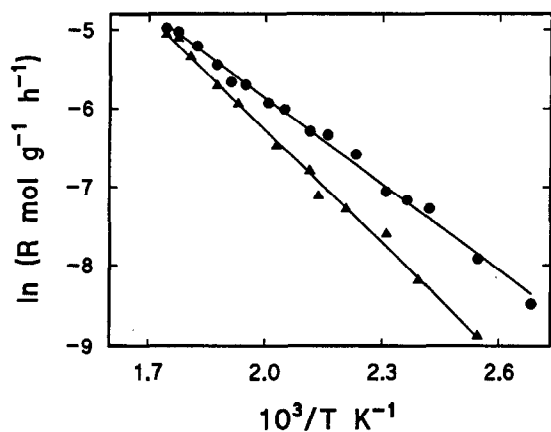


Fig. 5. Apparent Arrhenius plots for the isomerization of 1-hexene over $\text{MoO}_3/\text{Al}_2\text{O}_3$ (MOVS) (●) and the commercial molybdena catalyst (▲).

trated in Fig. 4 where the activity was unaffected by switching from a helium to a nitrogen carrier gas as was observed by Kovacs et al. [12]. The reaction can therefore be considered zero order with respect to the hydrocarbon concentration and the experimental reaction rates that were largely time invariant were taken as being equivalent to the reaction rate constant. The variation of logarithmic rate with reciprocal temperature yields the Arrhenius plots shown in Fig. 5. The computed apparent activation energy with 95% confidence limit for the isomerization of 1-hexene over $\text{MoO}_3/\text{Al}_2\text{O}_3$ (MOVS) is $30 \pm 1 \text{ kJ mol}^{-1}$. The commercial catalyst exhibited the same time-on-stream behaviour as the MOVS system but generated isomerization rates that were consistently lower as illustrated in Fig. 5 where the associated E_{app} ($40 \pm 2 \text{ kJ mol}^{-1}$) is appreciably higher. Catalytic activity in the isomerization of olefins has largely been attributed to surface Brønsted acidity and the isomerization of 1-hexene to 2-hexene proceeds via deprotonation from the adsorbed carbenium ion [17,18]. The impregnation of alumina with MoO_3 is known to generate Brønsted acid sites [16,19–21] while the alumina support alone exhibits only Lewis acidity [19,21]. The surface of alumina is generally accepted to be populated

with small molybdena clusters [22] and the electronegativity of alumina is altered in the vicinity of these clusters to generate the Brønsted acid sites [21]. The enhanced isomerization activities achieved using the laboratory prepared catalyst can not be attributed merely to a higher surface area but may be accounted for by the unique structural properties of the MOVS system. The unsupported MOVS precursor has been shown to possess 'dual dioxo molybdenum sites' and the unique bridging Mo–O–Mo moieties persist after its deposition on the support and calcination [3,4]. Earlier ESR data revealed a strong presence of similar Mo^{5+} ions in the supported and unsupported MOVS samples both before and after testing [4]. The g tensor values (2.445, 1.970, 1.940, 1.881 and 1.863) for the used catalysts are characteristic of both a mild reduced-distorted square pyramidal and strongly reduced-distorted octahedral Mo^{5+} coordination [23]. In contrast, it is known that Mo(VI) species predominate on the surface of calcined catalysts prepared by impregnation [24]. The infrared spectrum of the activated unsupported MOVS sample also reveals its distinct nature: bands at 990, 880 and 650 cm^{-1} imply lower coordination number(s) are present than is the case with octahedral $\alpha\text{-MoO}_3$ which is characterized by bands at 1000, 800 and 490 cm^{-1} [25]. The coordinatively unsaturated molybdenum species in the MOVS sample can therefore be expected to interact more strongly with the alumina support thereby modifying the surface Brønsted acidity to a greater extent and generating a more energetically favourable pathway for the isomerization of the adsorbed olefin. In addition, a slight reduction of supported molybdenum in the presence of olefins under catalytic conditions has been shown to occur [16] where the number of surface Brønsted acid sites is increased at a low extent of reduction [21]. The Mo–O–Mo linkages that are present on the MOVS surface are reduced more easily than the terminal Mo=O species [26] which suggests that the molybdenum component is more susceptible to reduction than is the case with the

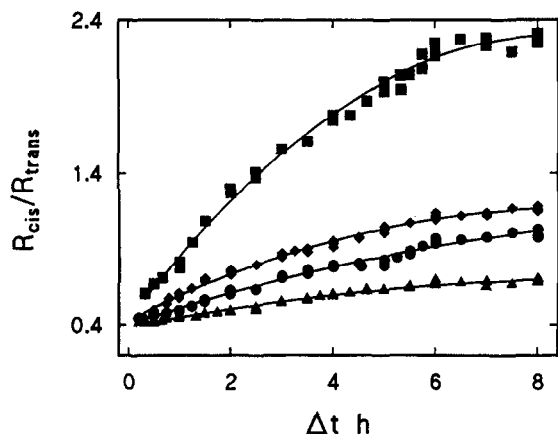


Fig. 6. Dependence of the rate ratio of *cis/trans* 2-hexene formation over $\text{MoO}_3/\text{Al}_2\text{O}_3$ (MOV5) with time-on-stream at 413 K (■), 473 K (◆), 523 K (●) and 573 K (▲) where the solid lines represent second order polynomial fits.

commercial catalyst. The more facile reduction of the bridging moieties during catalysis may produce an increase in the number of alumina hydroxyl groups near the molybdena clusters which constitute additional Brønsted acid sites again due to the inductive effects of molybdena on alumina [21].

The ratio of the rates of *cis/trans* 2-hexene formation was also dependent on the progress of the reaction and the variation of the rate ratio with time-on-stream is shown in Fig. 6. At every temperature the *cis* isomer was preferentially formed with increasing time. The experimental data obey a second order polynomial (the solid lines in Fig. 6) where the extrapolated values of $R_{\text{cis}}/R_{\text{trans}}$ (at $\Delta t = 0$ h) equal 0.40 ± 0.05 which agrees with the experimentally derived range of thermodynamic equilibrium values [27]. Departure from the equilibrium isomeric composition coincides with the observed drop in the degree of conversion and it is concluded that both phenomena stem from a common source. The buildup of surface carbon deposits must lower the available active surface area and cause a crowding effect where the adsorbed molecule adopts a geometry which is different from that of lowest energy in the isolated molecule. Based on the observed time dependence of product composition the steric hindrance induced by the presence of carbonaceous residues favours the formation of the *cis*

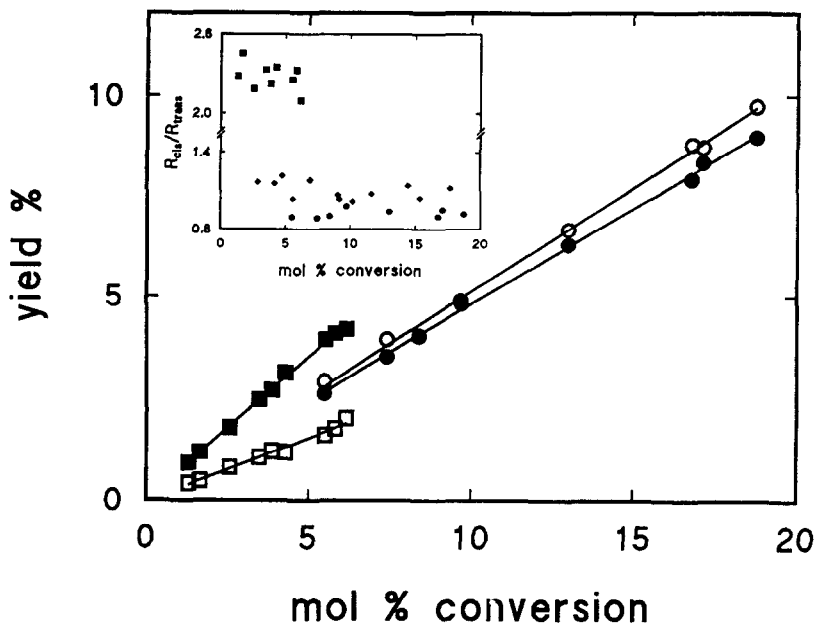


Fig. 7. Yield of *trans* (open symbol) and *cis* (closed symbols) 2-hexene as a function of conversion at 413 K (□, ■) and 523 K (○, ●). Inset: variation of the rate ratio of *cis/trans* 2-hexene formation with conversion at 413 K (■), 473 K (◆) and 523 K (●).

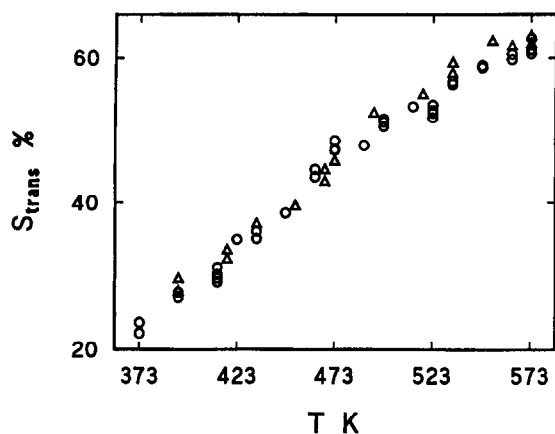


Fig. 8. Effect of temperature on the selective formation of *trans*-2-hexene over $\text{MoO}_3/\text{Al}_2\text{O}_3$ (MOVS) (O) and the commercial molybdena catalyst (Δ).

isomer. The yield of both isomers with increasing 1-hexene conversion is shown in Fig. 7, where the plotted activities correspond to a range of catalyst weights and reactant concentrations within the W/F interval 15–94 g h mol^{-1} . The yield of the *cis* and *trans* products is directly proportional to the degree of conversion of the reactant and both isomers can be considered primary products resulting from the direct surface catalysed isomerization of 1-hexene. Indeed the *cis/trans* ratios plotted in the inset to Fig. 7 exhibit no discernible dependence on percentage mol conversion. Interconversion of either isomer on the catalyst can therefore be discounted. Stereospecificity, in terms of the selective formation of the *trans* isomer, is displayed as a function of temperature in Fig. 8. The *trans* isomer was formed with increasing preference as the reaction temperature was elevated from 373 to 573 K. The commercial catalyst exhibited similar stereospecific behaviour to the MOVS system which suggests that the same stereo-differentiation mechanism applies to both systems. The ultimate product isomeric mixture only approaches the equilibrium composition at the highest reaction temperatures. It may be assumed that the surface constraints evident at lower temperatures are progressively relieved with increasing

temperature and this translates into an increasing preferential formation of the *trans* isomer.

4. Conclusions

The gas phase isomerization of 1-hexene over $\text{MoO}_3/\text{Al}_2\text{O}_3$ (MOVS) in a continuous flow reactor at $373 \text{ K} \leq T \leq 573 \text{ K}$ (a) proceeds with negligible internal or external diffusion constraints in the W/F range 14–81 g h mol^{-1} where the activity as a function of time can be represented by second order polynomial fits, (b) exhibits zero order dependency on 1-hexene concentration, identical rates in nitrogen or helium and an apparent activation energy of $30.4 \pm 1.3 \text{ kJ mol}^{-1}$, (c) is characterized by a marked initial drop in the degree of conversion particularly at lower temperatures but near identical activity/time-on-stream profiles are observed after catalyst regeneration, (d) yields higher rates than a commercial catalyst of equivalent loading as a result of the greater molybdena/alumina interaction due principally to the presence of bridging Mo–O–Mo moieties on the MOVS surface and (e) initially generates the expected *cis/trans* 2-hexene thermodynamic equilibrium as a result of the direct conversion of 1-hexene with negligible isomer interconversion but the isomeric ratio is shifted in favour of the *cis* form due to steric constraints induced by the presence of irreversibly adsorbed carbon species.

Acknowledgements

This research was funded by a grant from the Institute of Chemical Science and Technology.

References

- [1] J. Haber, in H.F. Barry and P.C.H. Mitchell (Eds.), Proceedings of the 3rd International Conference on the Chemistry and Uses of Molybdenum, Ann Arbor, MI, 1979, Climax Molybdenum Co., Ann Arbor, MI, 1979, p. 114.
- [2] F.E. Massoth, Adv. Catal., 27 (1979) 265.

- [3] E.C. Alyea, K.F. Brown, K.J. Fisher and K.D.L. Smith, *Stud. Surf. Sci. Catal.*, 75 (1993) 503.
- [4] E.C. Alyea and K.F. Brown, *Stud. Surf. Sci. Catal.*, 73 (1992) 279.
- [5] E.C. Alyea, K.F. Brown and K.J. Fisher, *J. Mol. Catal.*, 63 (1990) L11.
- [6] E.C. Alyea, K.F. Brown, L. Durham and I Svazic, *Stud. Surf. Sci. Catal.*, 73 (1992) 309.
- [7] E.C. Alyea, D. He and J. Wang, *Appl. Catal. A*, 104 (1993) 77.
- [8] J. Abbot and B.W. Wojciechowski, *J. Catal.*, 90 (1984) 270.
- [9] J. Abbot, A. Corma and B.W. Wojciechowski, *J. Catal.*, 92 (1984) 182.
- [10] J.R. Anderson, Y.F. Chang and R.J. Western, *J. Catal.*, 118 (1989) 466.
- [11] S. Saim and B. Subramaniam, *J. Catal.*, 131 (1991) 445.
- [12] J. Kovacs, G. Speier and L. Marko, *Inorg. Chem. Acta.*, 4 (1970) 412.
- [13] X.J. Li, J.H. Omiferko and B.C. Gates, *J. Catal.*, 85 (1984) 176.
- [14] X.J. Li, B.C. Gates, H. Knözinger and E.A. Delgado, *J. Catal.*, 88 (1984) 355.
- [15] K.F. Brown, M.Sc. Thesis, University of Guelph (1989).
- [16] J. Goldwasser, J. Engelhardt and K.W. Hall, *J. Catal.*, 70 (1981) 275; *ibid.*, 71 (1981) 381.
- [17] I.M. Campbell, *Catalysis at Surfaces*, Chapman and Hall, New York, 1988.
- [18] H. Pines, *The Chemistry of Catalytic Hydrocarbon Conversions*, Academic Press, New York, 1981.
- [19] F.E. Kiviat and L. Patrakis, *J. Phys. Chem.*, 77 (1973) 1232; *ibid.*, 78 (1974) 2070.
- [20] P. Ratnasamy, D.K. Sharma and L.D. Sharma, *J. Phys. Chem.*, 78 (1974) 2069.
- [21] W. Suarez, J.A. Dumesic and C.J. Hill, Jr., *J. Catal.*, 94 (1985) 408.
- [22] W.K. Hall, in H.F. Barry and P.C.H. Mitchell (eds.), *Proceedings of the 4th International Conference on the Chemistry and Uses of Molybdenum*, Golden, Colorado, 1982, Climax Molybdenum Co., Ann Arbor, MI, 1982, p. 224.
- [23] J. Haber, *ACS Symp. Ser.*, 279 (1985) 1.
- [24] E.C. Alyea and K.D.L. Smith, unpublished results.
- [25] Y. Iwasawa, S. Ogasawara, Y. Satao and H. Kuroda, in H.F. Barry and P.C.H. Mitchell (eds.), *Proceedings of the 4th International Conference on the Chemistry and Uses of Molybdenum*, Golden, Colorado, 1982, Climax Molybdenum Co., Ann Arbor, MI, 1982, p.283.
- [26] C. Li, K. Wang, Q. Xin and X. Guo, *Acta. Phys.-Chim. Sin.*, 8 (1992) 64.
- [27] R. Maurel, M. Guisnet and L. Bove, *Bull. Soc. Chim. Fr.*, (1969) 1975.