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Hydrogen production in the conversion of 2-methylbutane over a series of acid catalysts

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Abstract

The production of hydrogen from the conversion of 2-methylbutane was studied over a series of acid catalysts in a recirculation reactor system. Conversion of 2-methylbutane over an amorphous silica–alumina catalyst and ZSM-5 zeolite resulted in significant amounts of hydrogen. This supports a carbonium ion mechanism with a penta-coordinated carbonium ion intermediate. The conversion of 2-methylbutane over the USY zeolite and sulfated zirconia did not result in hydrogen being produced thus supporting the bimolecular carbenium ion mechanism. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Several mechanisms are accepted in the catalytic conversion of hydrocarbons over acid catalysts. These include the classical carbenium ion mechanism [1], carbonium ion mechanism [2], oligomerization followed by cracking [3–7], or a combination of these mechanisms depending on operating conditions [2,5,8–11]. These mechanisms differ by the proposed intermediates and product distributions. The classical carbenium ion mechanism is bimolecular and incorporates a carbenium ion intermediate [1,2]. For the isomerization of butane and the cracking of C_5 and larger hydrocarbons a cyclopropyl structured carbonium ion intermediate has also been proposed following the classical mechanism sequence of steps [4,12–14]. Propagation steps for this mechanism include β-scission and hydride transfer. Initiation involves hydride abstraction [15]. The production of molecular hydrogen is not expected, but is expected in the monomolecular carbonium ion mechanism. The proposed carbonium ion intermediate for the monomolecular mechanism consists of a penta-coordinated carbon with a three-centered two electron bond as shown in Fig. 1 [2,16]. A proton is added to the alkane for the initiation step [15].

One of the difficulties in separating these mechanisms is the complicated product distribution. At higher conversions the products of the more likely bimolecular mechanism can mask those of the monomolecular mechanism [8]. The same catalyst can exhibit either mechanism depending on reaction conditions. Haag and Dessau [2] summarized their work with the bimolecular mechanism being favored at high conversions and hydrocarbon partial pressures and low temperature. Hydrogen is a dominant product for the

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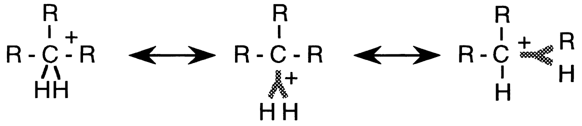

Fig. 1. Forms of carbonium ion intermediate.

monomolecular mechanism, but not for the bimolecular mechanism [2]. So, monitoring the production of hydrogen can aid in the determination of the mechanism taking place or the contribution of the monomolecular reaction. In a study of *n*-hexane and 2-methylpentane over HY zeolite, hydrogen was observed as a primary product in the case of the branched paraffin where hydride extraction would be easier than for the straight paraffin [17]. The monomolecular and bimolecular mechanism has been distinguished for butane, hexane, and 3-methylpentane cracking [2,10,18]. The goal of this research was to determine the possibility of each mechanism through the measurement of hydrogen production for 2-methylbutane conversion over a series of acid catalysts including amorphous silica–alumina, ZSM-5 and USY zeolites, and sulfated zirconia.

2. Experimental

2.1. Materials

The hydrocarbon reactant used in this study was 2-methylbutane supplied from Aldrich and used without further purification. Minor impurities included *n*-pentane and iso-butane (<0.15%). This hydrocarbon was chosen for being the simplest species having three types of hydrogen bonds and three types of carbon bonds.

The acidic catalysts included in these experiments were amorphous silica–alumina, ZSM-5 and USY zeolites, and sulfated zirconia. W.R. Grace manufactured the 135X amorphous silica–alumina catalyst with BET surface area of 380 m^2/g. To test pretreatment and regeneration conditions, dry or wet oxygen was used for pretreatment and regeneration at 550°C. The zeolites were supplied by United Catalyst and were exchanged from their ammonium form and calcined. Pretreatment was done with oxygen at 500°C and 525°C, respectively, for the ZSM-5 and USY zeolite. BET surface areas were 305 m^2/g for ZSM-5 and 270 m^2/g for the USY. The University of Kentucky Center for Applied Energy Research produced the sulfated zirconia catalyst with 213 m^2/g surface area. The sulfated zirconia was calcined in situ at 650°C under oxygen and the temperature reduced to reactor temperature under vacuum conditions.

2.2. Equipment and procedures

Experiments were conducted in the glass recirculation reactor system shown in Fig. 2 with either a pyrex reactor (silica/alumina and ZSM-5) or quartz reactor (USY and sulfated zirconia). Different system configurations were employed using traps of different volumes for direct sampling of either 1 l or 0.15 l within the circulation loop. Recirculation was achieved by a metal bellows pump. This system is similar to that used by Garten [19]. For on-line analysis of hydrogen, a multi-port valve injected a 1 ml sample into a Carle Analytical Gas Chromatograph 111 with a 10 ft×1/8 in. Hayesep D 100/120 mesh packed column and thermal conductivity detector. The analysis was performed isothermally at 30°C with 20 cm^3/min nitrogen as the carrier gas. Hydrocarbon analyses were performed on a Hewlett Packard 5890 Series II Gas Chromatograph with a 60 m×0.32 mm ID DB-5 column held at 10°C and fluid ionization detector. Samples collected during some of the sulfated zirconia experiments were also subject to sulfur analysis performed by the same HP with a Supelco SPB-1 30 m×0.32 mm i.d. column and a Sievers 350 B Sulfur Chemiluminescence Detector.

3. Results and discussion

3.1. Amorphous silica–alumina catalyst

The first run series compares the cracking of the 2-methylbutane over the silica–alumina catalyst at 350°C with, and without a platinum on activated carbon catalyst present in the recirculation system for reducing the product olefins. As shown in Fig. 3 hydrogen production was significant in the first case but not in the second. In additional experiments when

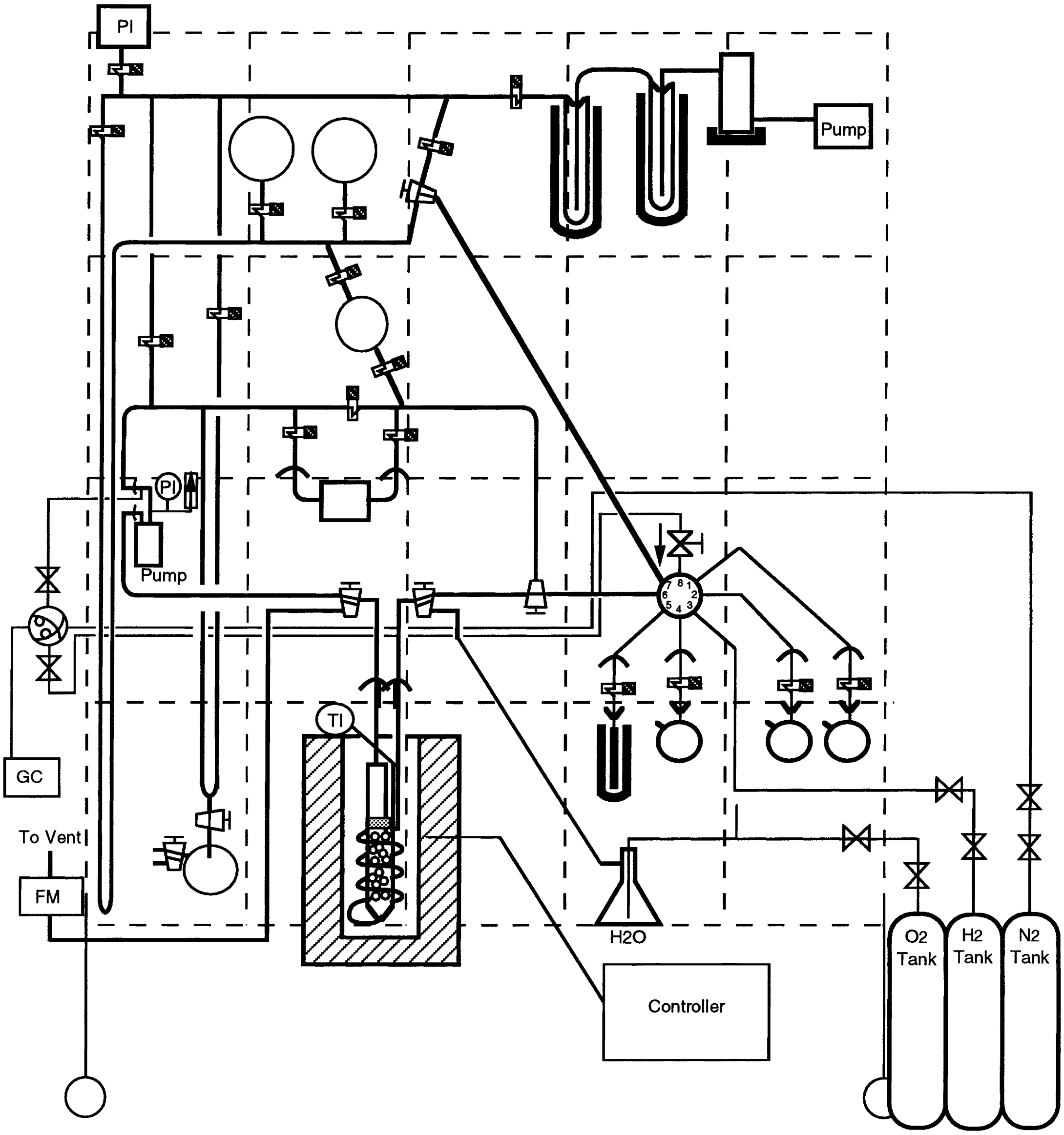

Fig. 2. Experimental system.

the platinum catalyst was in place, and hydrogen was added to the system there was a further reduction of olefins and a decrease in conversion. The presence of olefins in the product indicates the bimolecular mechanism, yet with the production of hydrogen the monomolecular mechanism is also involved.

In a second run series, catalyst regeneration and pretreatment conditions are compared for conversion at 350°C with a system volume of 1.15 l. Wet regeneration and pretreatment were achieved by bubbling the oxygen through a water trap prior to passing over the catalyst. There is not a large difference in conversion or hydrogen production between the wet or dry regeneration and pretreatment conditions as shown in Fig. 4.

In the last series, the system configuration is varied to yield catalyst to volume ratios of 8.7, 10, and 33.3 g/l. The hydrogen production does not directly

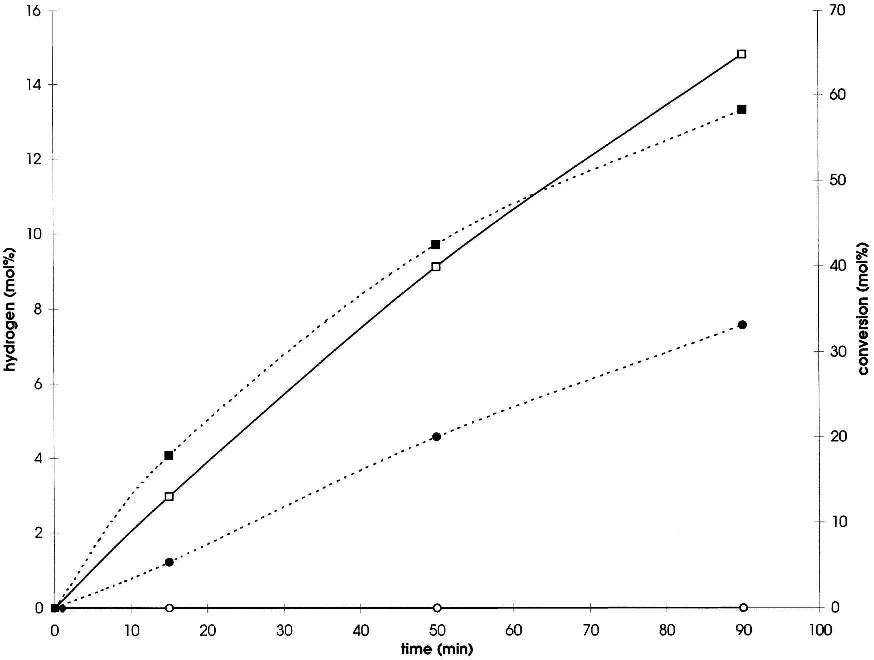

Fig. 3. Hydrogen production and conversion for amorphous silica alumina catalyst and in the presence of platinum on activated carbon. Hydrogen production (□) and conversion (■) at 350°C and the hydrogen production (○) and conversion (●) with platinum on activated carbon in the recirculation system.

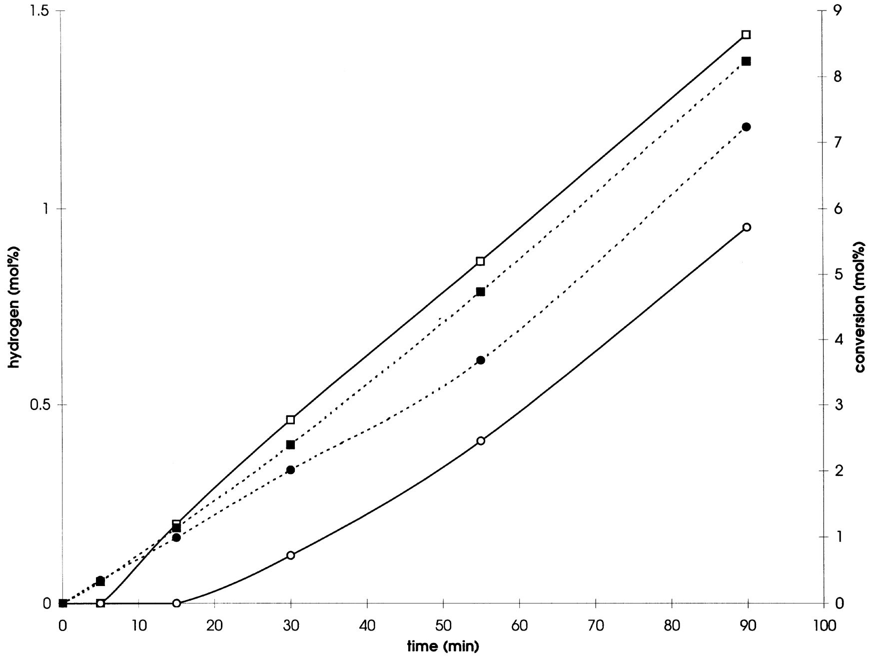

Fig. 4. Hydrogen production and conversion for amorphous silica–alumina catalyst undergoing different regeneration and pretreatment conditions. Hydrogen production (□) and conversion (■) with dry regeneration and pretreatment and hydrogen production (○) and conversion (●) with wet regeneration and pretreatment.

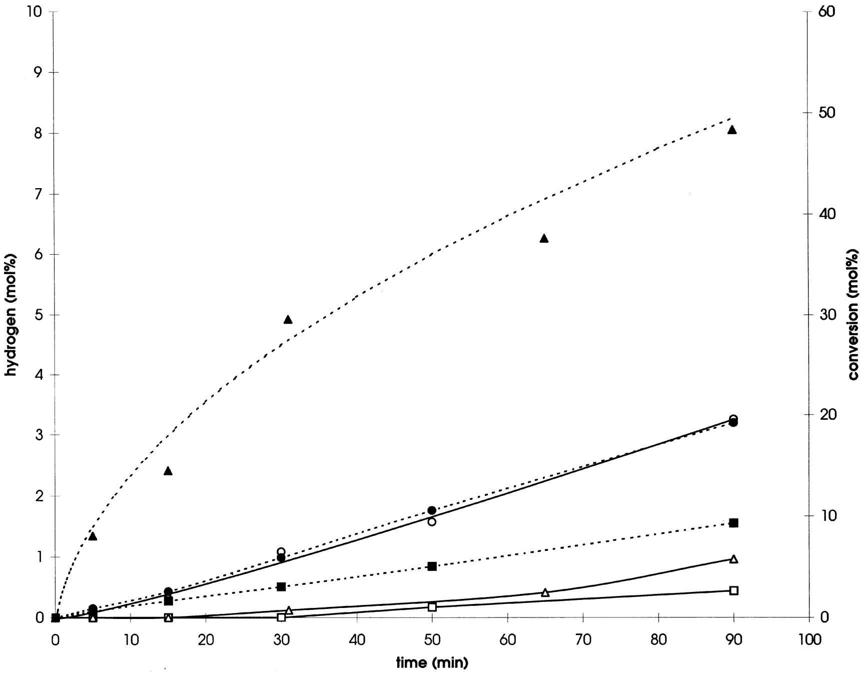

Fig. 5. Hydrogen production and conversion for amorphous silica alumina catalyst with different catalyst to reactor volume ratios. Hydrogen production (□) and conversion (■) with 8.7 g/l, hydrogen production (○) and conversion (●) with 10 g/l, and hydrogen production (△) and conversion (▲) with 33.3 g/l.

follow the increase in conversion as the catalyst to volume ratio is increased as shown in Fig. 5. The largest amount of hydrogen is produced when the catalyst to volume ratio is 10 g/l.

3.2. Zeolites (ZSM-5 and USY)

The first run series for ZSM-5 shown in Fig. 6 were conducted at 350°C and 250°C. The production of hydrogen decreases with the decrease in reaction temperature. Similar to the amorphous silica–alumina catalyst, the presence of Pt on C resulted in a decrease in hydrogen production as shown in Fig. 7.

Conversions of 2-methylbutane over USY at different reactor temperatures ranging from 250°C to 150°C are presented in Fig. 8. No hydrogen was detected in any of the product samples. Fig. 9, shows conversions at 200°C for system configurations of 0.87 and 3.33 g/l. Again no hydrogen was detected.

ZSM-5 under these conditions can be considered to favor the monomolecular mechanism, whereas USY would favor the bimolecular mechanism. From the difference in pore sizes between these two zeolites this can be accepted. USY with the larger pore size can better accommodate the larger bimolecular intermediates.

3.3. Sulfated zirconia

Conversion of 2-methylbutane over the sulfated zirconia catalyst at 250°C resulted in nearly 100% conversion and production of large amounts of coke and sulfur compounds, H_2S, COS, and SO_2. The conversion at different temperatures of 250°C and 100°C is shown in Fig. 10 for a flow of 13.3 g/l. Fig. 11 shows conversion results at 100°C and 50°C for a system configuration of 0.87 g/l. The system configurations of 13.3 and 0.87 g/l are shown in Fig. 12. No hydrogen was detected in any of the sulfated zirconia runs. Sulfur analysis of experiments run at 150°C and 6.7 g/l showed only trace amounts of sulfur compounds (less than 5 ppm). On the basis of hydrogen production, sulfated zirconia would be assumed to proceed via the bimolecular mechanism.

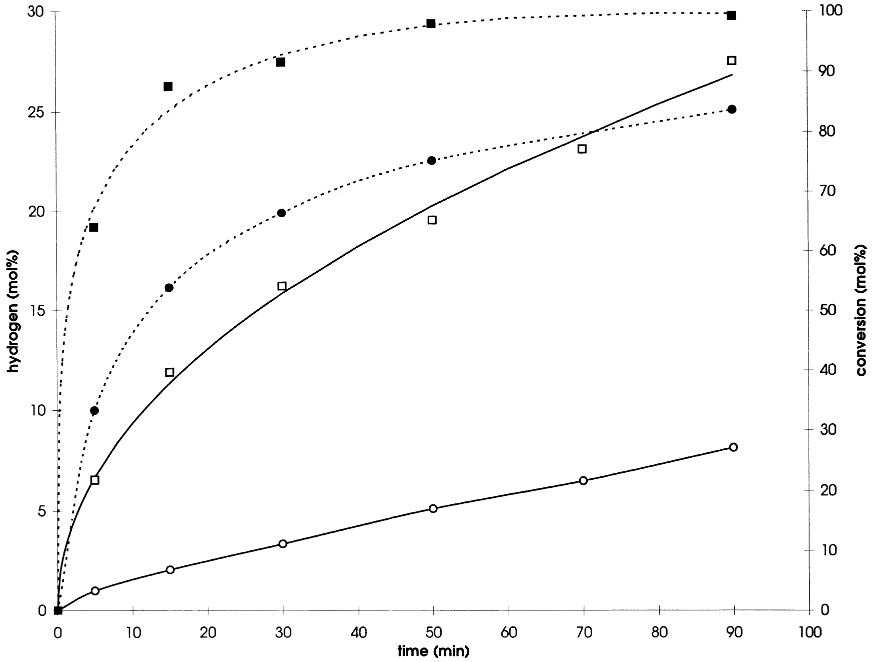

Fig. 6. Effect of temperature on ZSM-5. The hydrogen production (□) and conversion (■) at 350°C and hydrogen production (○) and conversion (●) at 250°C.

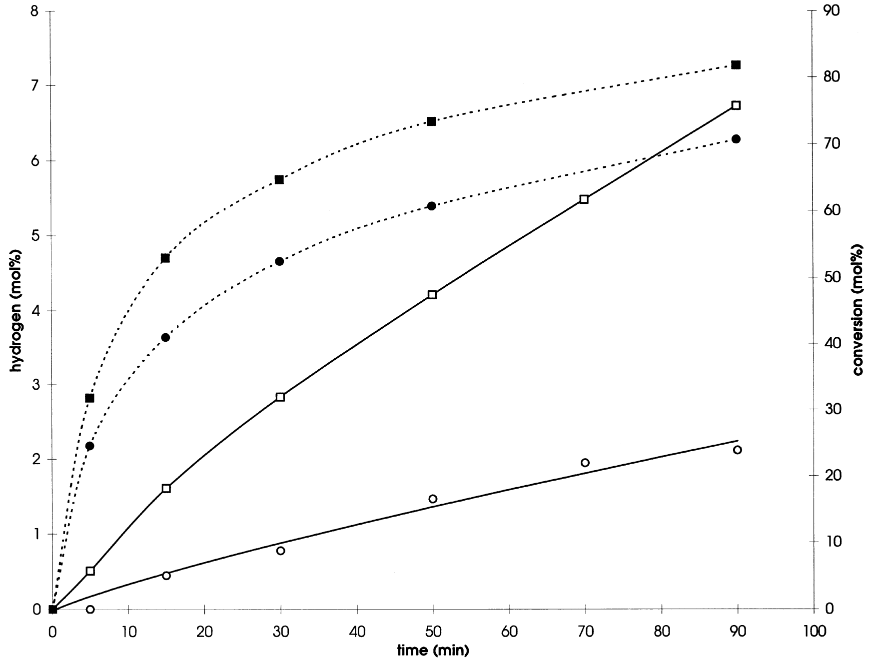

Fig. 7. Pt on C effect on hydrogen production and conversion over ZSM-5. Hydrogen production (□) and conversion (■) at 250°C and hydrogen production (○) and conversion (●) at 250°C with Pt on C.

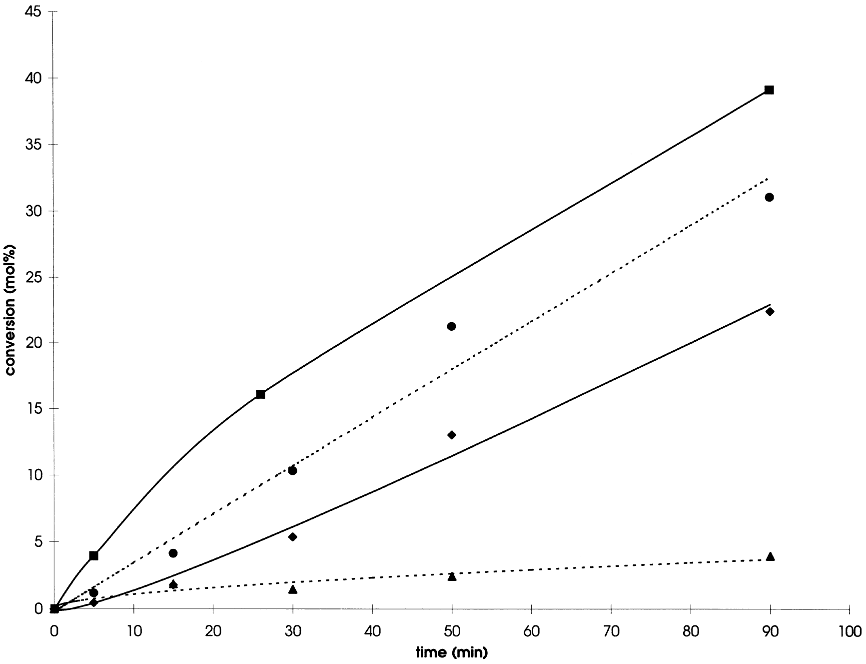

Fig. 8. Conversion over USY at different temperatures with no resulting hydrogen production. Conversion at 250°C (■), 200°C (●) and (◆), and 150°C (▲).

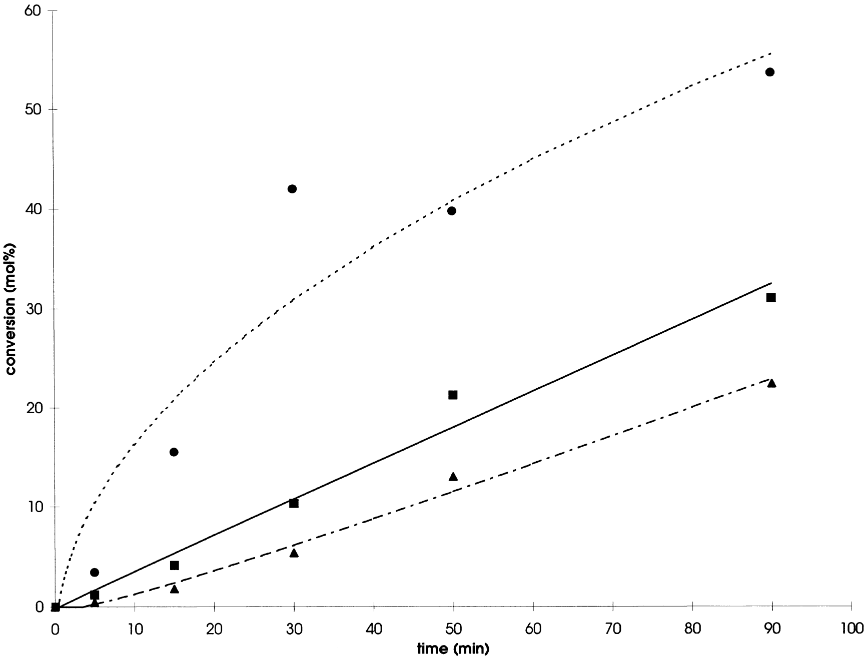

Fig. 9. Conversion over USY with different configurations at 200°C. Conversion at 0.87 g/l (■) and (▲), and 3.33 g/l (●).

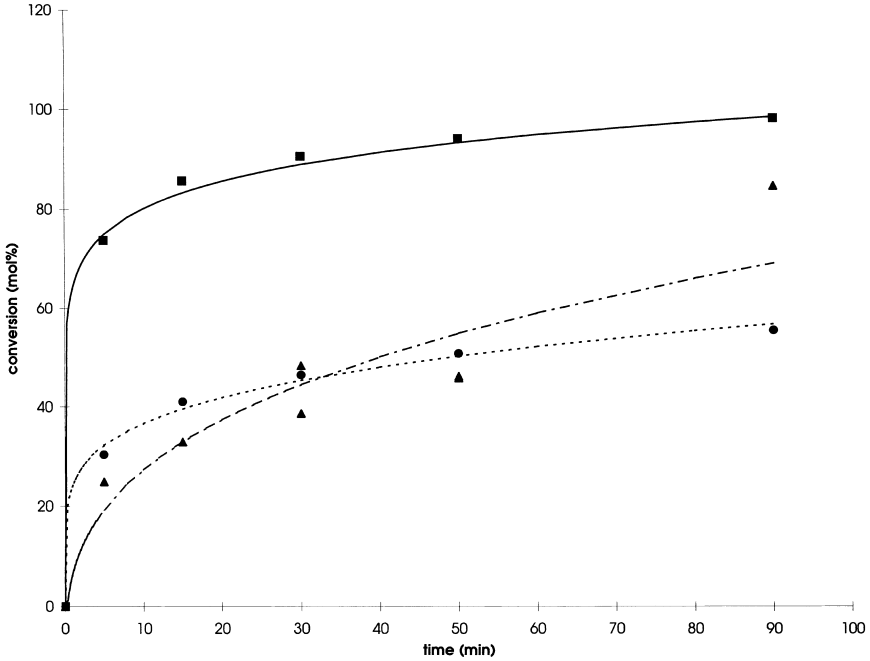

Fig. 10. Conversion over sulfated zirconia at different temperatures. Conversion at 250°C (■) and 100°C (▲), and (●).

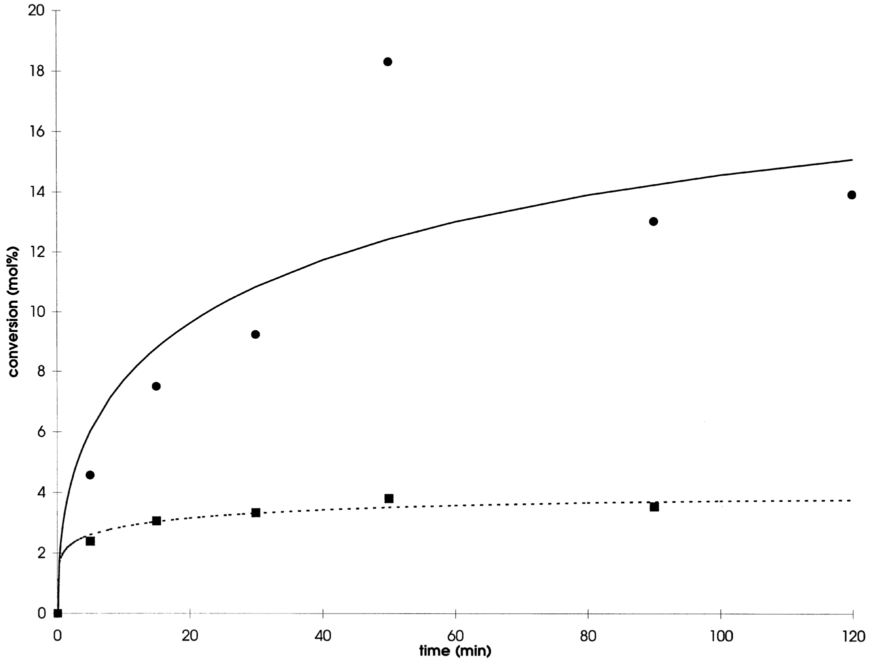

Fig. 11. Conversion over sulfated zirconia at different temperatures with 0.87 g/l. Conversion at 50°C (■) and 100°C (●).

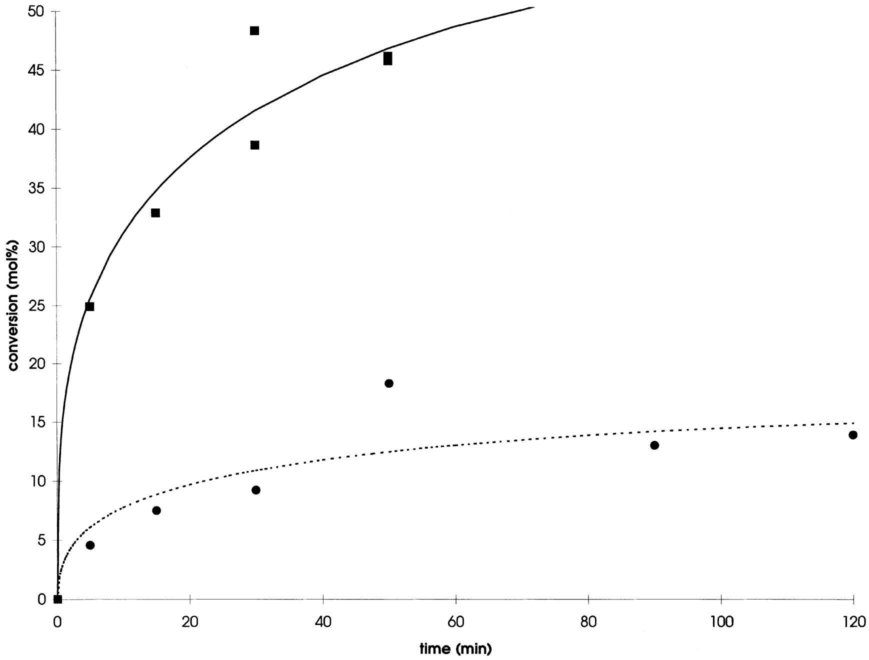

Fig. 12. Conversion over sulfated zirconia at different system configurations at 100°C. Conversion at configurations of 13.3 g/l (■) and 0.87 g/l (●).

4. Conclusions

For the amorphous silica–alumina catalyst, hydrogen is produced under all conditions except in the presence of platinum on activated carbon. ZSM-5 also has significant hydrogen production at various conditions studied. The use of platinum on activated carbon resulted in a significant decrease in the production of hydrogen for the amorphous silica–alumina and ZSM-5 catalysts. Neither USY nor sulfated zirconia ever produced measurable amounts of hydrogen under the range of conditions studied.

On the basis of hydrogen production, the monomolecular mechanism involving a carbonium ion intermediate, such as the penta-coordinated carbonium ion, participates in the conversion of 2-methylbutane over the amorphous silica–alumina and ZSM-5 catalysts. A reaction pathway that does not produce hydrogen must be coupled with the carbonium mechanism. Over the USY and sulfated zirconia catalyst conversion takes place via the bimolecular mechanism incorporating the various carbenium ion or cyclopropyl type intermediates. Presumably the differences among these catalysts is caused by differences in the nature of the anion.

Acknowledgements

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References

[1] B.S. Greensfelder, H.H. Voge, G.M. Good, Ind. Eng. Chem. 41 (1949) 2573.

[2] W.O. Haag, R.M. Dessau, in: Proceedings of the Eighth International Congress on Catalysis, vol. II, Verlag Chemie, Berlin, 1984, p. 305.

[3] R. Shigeishi, A. Garforth, I. Harris, J. Dwyer, J. Catal. 130 (1991) 423.

[4] G.A. Olah, O. Farooq, A. Husain, N. Ding, N.J. Trivedi, J.A. Olah, Catal. Lett. 10 (1991) 239.

[5] J. Engelhardt, W.K. Hall, J. Catal. 125 (1990) 472.
[6] Y.V. Kissin, J. Catal. 146 (1994) 358.
[7] G. Yaluris, J.E. Rekoske, L.M. Aparicio, R.J. Madon, J.A. Dumesic, J. Catal. 153 (1995) 65.
[8] S.J. Collins, P.J. O'Malley, J. Catal. 153 (1995) 94.
[9] E.A. Lombardo, W.K. Hall, J. Catal. 112 (1988) 565.
[10] H. Krannila, W.O. Haag, B.C. Gates, J. Catal. 135 (1992) 115.
[11] J. Abbot, B.W. Wojciechowski, Can. J. Chem. Engr. 63 (1985) 278.
[12] S.T. Sie, Ind. Eng. Chem. Res. 31 (1992) 1881.
[13] S.T. Sie, Ind. Eng. Chem. Res. 32 (1993) 397.
[14] S.T. Sie, Ind. Eng. Chem. Res. 32 (1993) 403.
[15] J.A. Lercher, R.A. van Santen, H. Vinek, Catal. Lett. 27 (1994) 91.
[16] G.A. Olah, J. Am. Chem. Soc. 94 (1972) 808.
[17] J. Abbot, B.W. Wojciechowski, J. Catal. 113 (1988) 353.
[18] J. Meusinger, J. Liers, A. Mosch, W. Reschetilowski, J. Catal. 148 (1994) 30.
[19] R.L. Garten, Ph.D. Thesis, The Johns Hopkins University, 1967.