Contributions of acid and metal sites to propane aromatisation over fresh Ga, H-ZSM-5 catalyst

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Abstract

A kinetic modelling has been developed to describe the aromatisation of propane over fresh H-ZSM-5 and Ga, H-ZSM-5 catalysts at 500°C. It was shown that the introduction of metal into H-ZSM-5 has enhanced both the yield and selectivity of aromatics and that the conversion of propane is mainly due to the dehydrogenation step over metal sites. Over Ga, H-ZSM-5 catalyst, the contribution of hydrogen transfer steps (between the feed alkane and alkenes adsorbed over acid sites) to the conversion of alkane is reduced considerably. On the other hand, the formation of aromatics is mainly from aromatisation steps over metal sites. As a result of the alkane dehydrogenation and alkene aromatisation steps over metal sites, the hydrogen yield is observed to increase in comparison with the hydrogen yield for the transformation over H-ZSM-5.

1. Introduction

The conversion of light alkanes into aromatic hydrocarbons is an important reaction from both the academic and industrial points of view. The medium pore zeolite ZSM-5 appears to be the most effective for this reaction [1]. The introduction of metal species, such as platinum, gallium or zinc, into H-ZSM-5 results in a remarkable enhancement of the catalyst aromatisation activity, but also leads to a pronounced increase in the rate of coke formation and related catalyst deactivation [2]. The enhancement of aromatisation activity on Me, H-ZSM-5 catalyst was attributed to the appearance of active metal sites as Lewis sites after the introduction of metal species into the zeolite [3, 4].

In agreement with the literature data [2, 5], the aromatisation of light alkane over ZSM-5 catalysts can be represented as a two-stage process: (i) transformation of light alkanes into light alkenes, and (ii) aromatisation of light alkenes. Over H-ZSM-5 catalysts, the first stage includes two routes: protolytic cracking route and hydrogen transfer route while the second stage proceeds through a number of acid-catalysed oligomerisation, cracking, cyclisation, and hydrogen transfer (HT) steps [5]. Over Me, H-ZSM-5 catalysts, metal species provide additional dehydrogenation routes for propane transformation into propene, and for alkenes transformation into aromatics [2, 5]. During the reaction, coke is also formed from reactive alkenes, covering active sites of the catalyst, and leading to catalyst deactivation [5, 8]. The entire pathway of the aromatisation reaction of light alkanes over H-ZSM-5 and

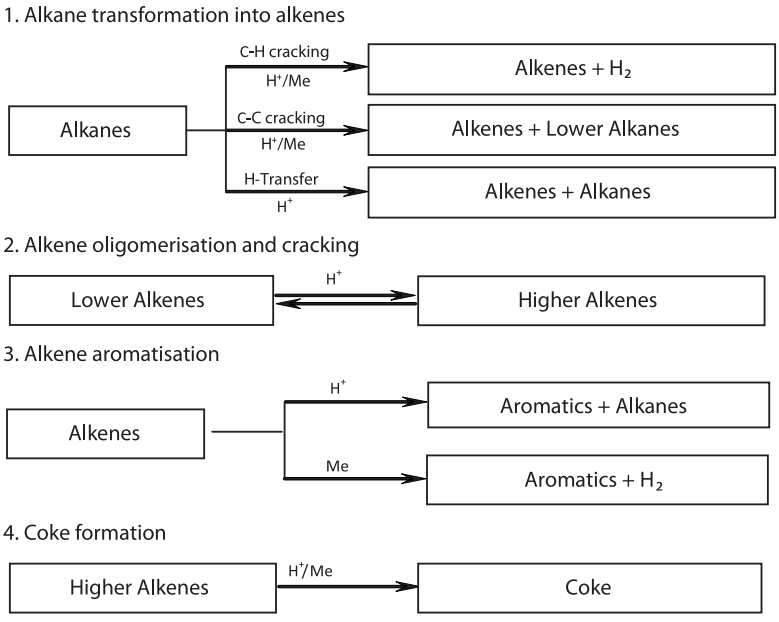

Fig. 1. *Reaction scheme of alkane aromatisation over Me, H-ZSM-5 catalysts*

Me, H-ZSM-5 catalysts is shown in Fig. 1. It is interesting to determine quantitative contributions of acid and metal sites to the reaction. In this work, we consider an approach to the development of a kinetic model that describes major features of the propane aromatisation over fresh H-ZSM-5 and Ga, H-H-ZSM-5 catalysts.

2. Experimental

H-ZSM-5 zeolite (Si/Al = 15) was used as a catalyst in this work. 1% Ga, H-ZSM-5 catalyst was prepared by impregnation of H-ZSM-5 zeolite with gallium nitrate solution using the incipient impregnation technique. Kinetic studies of propane reaction were performed at 500°C. The reactions were carried out under nondeactivating conditions at atmospheric pressure in a continuous flow micro-reactor with a feed of 80wt% of propane (N_2 was used as a gas carrier and diluting agent). Prior to the catalytic experiments, the catalyst samples were activated under N_2 flow (30ml/min) at 500°C for 4h. Reaction products were analysed by on-line GC equipped with two detectors: TCD (analysis of H_2) and FID (analysis of hydrocarbons). Different levels of conversions were obtained by performing experiments at different weight hour space velocities (WHSV) which have been checked for satisfaction of the reaction occurring in a kinetic regime. In our investigated conditions, at a certain space velocity, changes in flow rate and catalyst amount do not have any considerable effect on our experimental results. Hence, mass transfer limitation can be ignored.

3. Results and Discussion

3.1. Formulation of the model for the aromatisation of propane over fresh Ga, H-ZSM-5 catalysts.

The kinetic modelling to describe the reaction over a bifunctional catalyst (e.g. Ga, H-ZSM-5) is performed over two stages: (1) Development of a model for the reaction over H-ZSM-5 and (2) Modification of the model to apply for the reaction over Ga, H-ZSM-5. A model to describe the reaction of propane over H-ZSM-5 was developed and reported in our previous paper [6]. To apply the model for describing the reaction over a bifunctional catalyst, the reaction steps over metal sites and their corresponding rate constants and adsorption constants have been included into the model. According to a study by Turner [7], after introducing gallium species into H-ZSM-5, the number of Brönsted acid sites in a zeolite reduces by 60%. Therefore, over the bifunctional catalyst, the values of rate constants for reaction steps over acid sites, which have been obtained from the estimation over H-ZSM-5 catalyst, are multiplied by a factor of 0.4. Estimation of these values of rate constants is based on the comparison between the modelling results and experimental data on propane aromatisation over Ga, H-ZSM-5 catalyst at 500°C. A detailed procedure of the estimation for rate constants of the reaction steps over fresh H-ZSM-5 has been presented in our previous papers [6]. Hence, in this paper, only modelling results for the reaction steps over metal sites are reported (Table 1).

Table 1. *Relative values of rate constants for some reaction steps over metal sites in propane aromatisation over Ga, H-ZSM-5*

Reaction steps	Rate constants
$C_3 \rightarrow C_3^= + H_2$	1.0
$C_3^= + H_2 \rightarrow C_3$	12.7
$C_3 \rightarrow C_2^= + C_1$	0.21
$C_{6+}^= \rightarrow$ A (aromatics) + $2H_2$	64.0

From Table 1, the modelling results show that over metal sites, propane conversion by dehydrogenation is 4.8 times (1/0.21) higher than by cracking. Moreover, over metal sites, while propane dehydrogenation is reversible, C-C cracking of propane is irreversible. Therefore, it can be concluded that transformation of propane over metal sites is mainly from the route of dehydrogenation. It is shown that the rate of the reverse reaction of propane dehydrogenation (i.e., propene hydrogenation) is 12.7 times higher than that of propane dehydrogenation. Furthermore, it can be seen that over metal sites, the rate of $C_{6+}^=$ aromatisation (and also $C_{6+}^=$ dehydrogenation) is 64 times higher than that of dehydrogenation of propane.

In comparison with the reaction over H-ZSM-5, it can be seen that over Ga, H-ZSM-5, propane is converted 3 times faster than over H-ZSM-5 (Table 2). This result is comparable with the result reported by Lukyanov et al. (3.3 times) [5]. It is worth noting that the ratio between the rates of C-C cracking and C-H cracking decreases from 3 for H-ZSM-5 down to 0.3 for Ga, H-ZSM-5. Obviously, the dehydrogenation (or C-H cracking) becomes more favourable over Ga, H-ZSM-5 due to the contribution of metal sites to the mechanism for propane transformation.

Table 2. *Rate constants (mol g^{-1} atm^{-1} h^{-1}) for propane dehydrogenation and cracking steps over acid and metal sites for propane conversion over H-ZSM-5 and Ga, H-ZSM-5 catalysts at 500°C*

Reaction steps	H-ZSM-5	Ga, H-ZSM-5	
	H^+	H^+	Ga
$C_3 \rightarrow C_3^= + H_2$	0.013	0.0052	0.110
$C_3 \rightarrow C_2^= + C_1$	0.039	0.0156	0.023

3.2. Application of the model to describe the propane aromatisation over H-ZSM-5 and Ga, H-ZSM-5 catalysts at 500°C

The agreement between modelling results and experimental data is shown in Fig. 2 for the conversions of propane over H-ZSM-5 and Ga, H-ZSM-5 at 500°C. It can be seen that the model describes the experimental data properly. As expected, the conversion of propane increases with contact time. Fig. 2 shows that the conversions of propane over H-ZSM-5 and Ga, H-ZSM-5 catalysts are similar. It is worth to note that while the model describes propane transformation over H-ZSM-5 catalyst very well, its description over Ga, H-ZSM-5 shows an excess of alkane formation in comparison with experimental data (Fig. 3). However, main characteristics of the reaction are still reflected and description of main products (i.e., aromatics) is reasonable.

In other words, the introduction of gallium species into H-ZSM-5 has not changed the conversion of propane

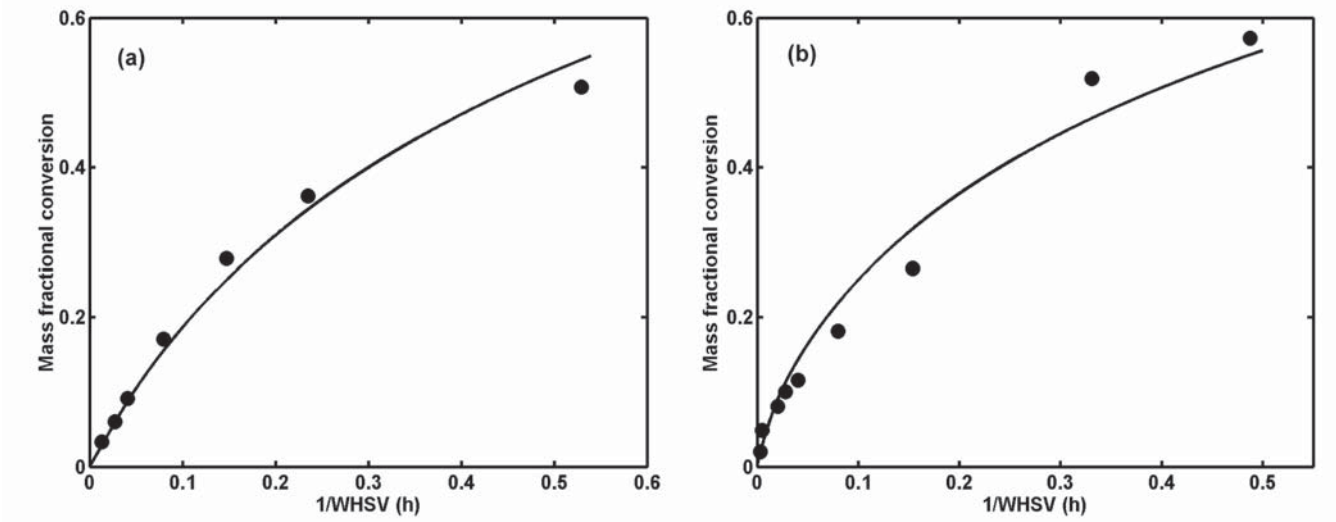

Fig. 2. *Propane aromatisation over fresh (a) H-ZSM-5 and (b) Ga, H-ZSM-5 at 500°C. Experimental data (points) and calculated curves for the conversion as a function of 1/WHSV*

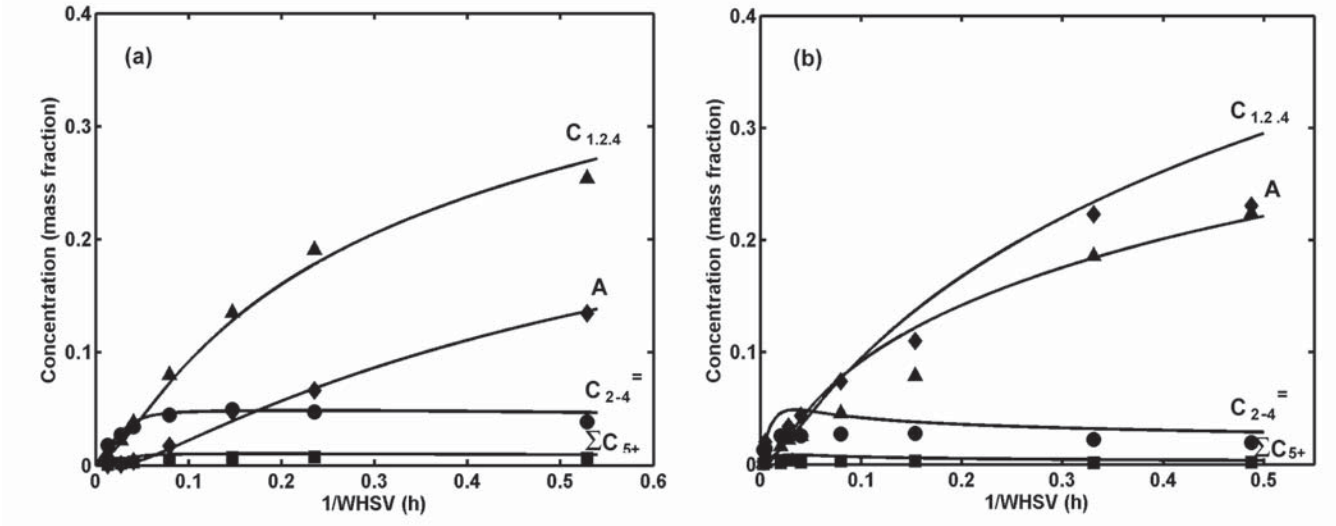

Fig. 3. *Propane aromatisation over fresh (a) H-ZSM-5 and (b) Ga, H-ZSM-5 at 500°C. Experimental data (points) and calculated curves for the concentrations of $C_{1,2,4}$ alkanes, $C_2^=$-$C_4^=$ alkenes, C_{5+} aliphatic hydrocarbons and aromatics as functions of 1/WHSV*

considerably. However, distribution of products in the reaction mixture is different due to the modification of the reaction pathway by the participation of reaction steps over metal sites into the transformation of propane into aromatics. Compared to the reaction over H-ZSM-5, over Ga, H-ZSM-5, a higher concentration of aromatics and lower concentrations of alkenes are observed as a result of a higher consumption of alkenes in aromatisation steps (Fig. 3). Effects of metal introduction on the reaction are discussed in the next section.

3.3. Effects of the introduction of metal species into catalyst on the reaction

3.3.1. The contribution of hydrogen transfer steps to conversion of propane

As discussed in our previous papers [6, 9], as the alkane conversion increases, the contribution of hydrogen transfer (HT) steps to the alkane transformation becomes significant and should be taken into account in the model for the reaction over H-ZSM-5. Modelling results in this work show that when mass fractional conversion of the alkane is around 0.50, this contribution is approximately 20% for propane aromatisation (Fig. 4). This result is in agreement with the result reported by Lukyanov et al. for propane aromatisation over H-ZSM-5 [5].

However, over Ga, H-ZSM-5, the contribution of hydrogen transfer steps between propane and alkenes adsorbed over acid sites is reduced considerably in comparison with over H-ZSM-5 (Fig. 5). Obviously, this reduction results from the addition of alkane conversion over metal sites and also from the decrease in the number of acid sites available for this reaction. In practice, at a propane mass fractional conversion of around 0.50, the contribution of these hydrogen transfer steps to the conversion of propane is only 2.8%. Therefore, it can be concluded that over Ga, H-ZSM-5, the conversion of propane mainly occurs by cracking and dehydrogenation steps over acid and metal sites.

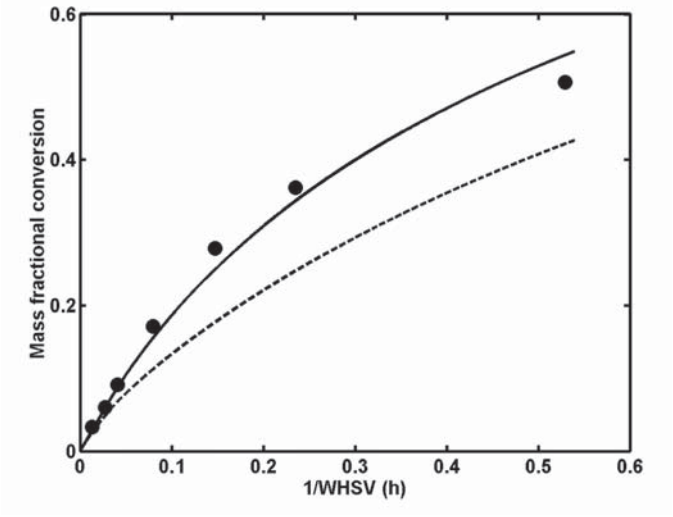

Fig. 4. *Propane aromatisation over fresh H-ZSM-5 at 500°C. Experimental data (points) and calculated curves (solid curve for the reaction over real catalyst with HT activity and dash curve for the reaction over pseudo-catalyst without HT activity) for propane conversion as a function of 1/WHSV*

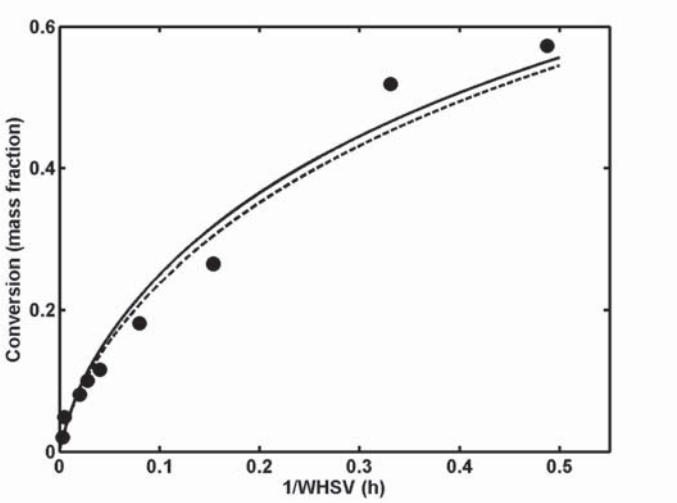

Fig. 5. *Propane aromatisation over fresh Ga, H-ZSM-5 at 500°C. Experimental data (points) and calculated curves (solid curve for the reaction over real catalyst with HT activity and dash curve for the reaction over pseudo-catalyst without HT activity) for propane conversion as a function of 1/WHSV*

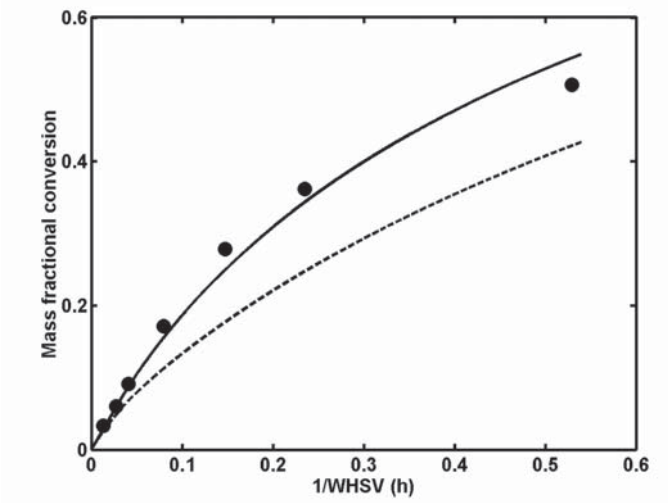

Fig. 6. *Propane aromatisation over fresh Ga, H-ZSM-5 at 500°C. Experimental data (points) and calculated curves (solid curve for the reaction over real catalyst with cracking activity over acid sites and dash curve for the reaction over pseudo catalyst without cracking activity over acid sites) for propane conversion as a function of WHSV-1*

3.3.2. The contribution of cracking steps over acid sites to propane conversion

In order to investigate the contributions of the cracking steps over acid sites of Ga, H-ZSM-5, a model without cracking steps over acid sites was constructed. On the basis of comparison of modeling results between the models over a real catalyst and over a pseudo-catalyst (without cracking activity over acid sites), it was shown that when the mass fractional conversion of propane is about 0.50, cracking steps over acid sites contribute approximately 7% to the conversion of propane over Ga, H-ZSM-5 (Fig. 6). Therefore, it can be concluded that over Ga, H-ZSM-5, propane activation is mainly catalysed by metal sites. This conclusion is also in agreement with the results reported by Lukyanov et al. for propane aromatisation over Ga, H-ZSM-5 [5].

3.3.3. Aromatisation steps over acid and metal sites

In comparison with propane transformation over H-ZSM-5, the introduction of metal into H-ZSM-5 has enhanced both the yield and selectivity of aromatics (Table 3). It can be seen from Table 3 that an enhancement of the aromatics yield is accompanied with a decrease in the alkane yield and an increase in the hydrogen yield. Therefore, it can be concluded that this enhancement arises from the dehydrogenation steps over metal sites, and not from the aromatisation steps over acid sites.

As a result of alkane dehydrogenation and alkene aromatisation steps over metal sites, the hydrogen yield is observed to increase in comparison with that obtained over H-ZSM-5 catalyst (Table 3). In addition, concentrations of alkenes, especially C_{6+} = alkenes, decrease sharply due to their intense consumption in the aromatisation steps (Fig.7).

It is also interesting to know the contribution of aromatisation steps over acid sites and over metal sites to the formation of aromatics over Ga, H-ZSM-5. Accordingly, a model without aromatisation steps over acid sites was constructed. On the basis of the comparison of the results obtained from the models with and without aromatisation activity over acid sites, it has been shown that at an alkane fractional conversion of around 0.50, these steps contribute less than 0.3% to the formation of aromatics over Ga, H-ZSM-5. In fact, this contribution can be neglected (Fig. 8). Hence, it can be concluded that over Ga, H-ZSM-5 catalyst, the formation of aromatics is mainly from the aromatisation steps over metal sites.

Table 3. *Calculated yield and selectivity of aromatics, yields of alkanes, alkenes, and hydrogen for propane conversion over H-ZSM-5 and Ga, H-ZSM-5 catalysts at 500°C and a mass fractional conversion of 0.30*

	H-ZSM-5	Ga,H-ZSM-5
Alkane yield	0.5200	0.4237
Alkene yield	0.1892	0.1437
Hydrogen yield	0.0092	0.0332
Aromatics yield	0.1831	0.3803
Aromatics selectivity	0.2119	0.4412

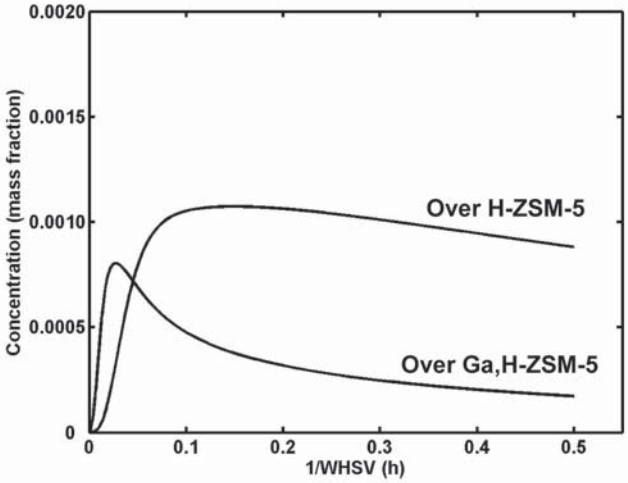

Fig. 7. *Propane aromatisation over fresh H-ZSM-5 and Ga, H-ZSM-5 at 500°C. Calculated curves for C_{6+} = concentration as a function of $WHSV^{-1}$*

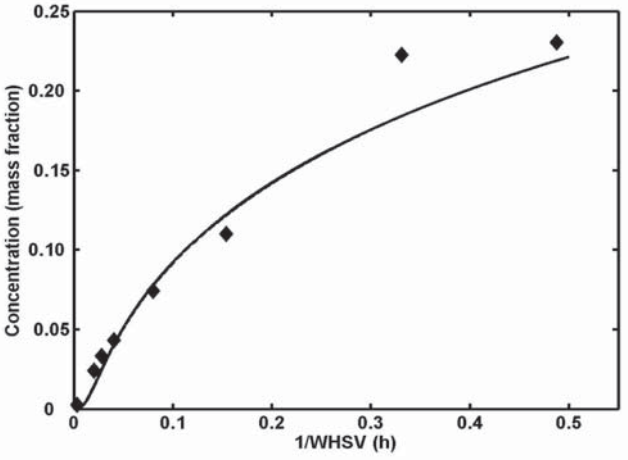

Fig. 8. *Propane aromatisation over fresh Ga, H-ZSM-5 at 500°C. Experimental data (points) and calculated curves (solid curve for the reaction over the real catalyst with aromatisation activity over acid sites and dash curve for the reaction over the pseudo-catalyst without aromatisation activity over acid sites) for the aromatics concentrations as a function of $WHSV^{-1}$*

4. Conclusions

The kinetic model developed in this work describes major features of propane aromatisation over fresh H-ZSM-5 and Ga, H-ZSM-5 catalysts at 500^0C properly. On the basis of the kinetic modelling results, it could be concluded that:

- Over Ga, H-ZSM-5, besides reaction steps over acid sites, additional steps over metal sites also contribute to the conversion of alkane and the formation of aromatics significantly. In comparison with the transformation performed over H-ZSM-5, the introduction of metal into H-ZSM-5 has enhanced both the yield and selectivity of aromatics. In addition, a decrease in the concentrations of alkenes due to their consumption in the aromatisation is also observed, and this decrease is more pronounced for the transformation of propane over Ga, H-ZSM-5 than over H-ZSM-5.

- Under the reaction conditions investigated, the rate of propane dehydrogenation over metal sites is 12.7 times slower than that of propene hydrogenation. On the other hand, the rate of propane cracking over metal sites is lower in comparison with propane dehydrogenation. Therefore, the transformation of propane over metal sites is mainly via the route of dehydrogenation.

- Over Ga, H-ZSM-5, the contribution of hydrogen transfer steps (between the feed alkane and alkenes adsorbed over acid sites) to the conversion of alkane is reduced considerably in comparison with that over H-ZSM-5. In fact, the conversion of propane is mainly due to the dehydrogenation step over metal sites.

- As a result of the alkane dehydrogenation and alkene aromatisation steps over metal sites, the hydrogen yield is observed to increase in comparison with that over H-ZSM-5. Over Ga, H-ZSM-5 catalyst, the formation of aromatics is mainly from the aromatisation steps over metal sites.

References

1. Fricke, R., Kosslick, H., Lischke, G., and Richter, M. *Incorporation of gallium into zeolites: Syntheses, properties and catalytic application*. Chem. Revs. 2000; 100: p. 2303 - 2405.

2. Kwak, B. S., Sachtler, W. M. H. and Hagg, W. O. Catalytic conversion of propane to aromatics: Effects of adding Ga and/or to HZSM-5. J. Catal. 1994; 149: p. 465 - 473.

3. Biscardi, J. A., and Iglesia, E. *Reaction pathways and rate-determining steps in reactions of alkanes on HZSM-5 and Zn/HZSM-5 catalysts*. J. Catal. 1999; 182: p. 117 - 128.

4. El-Malki, El-M., van Santen, R. A. and Sachtler, W. M. H., 1999. *Introduction of Zn, Ga, and Fe into HZSM-5 cavities by sublimation: Identification of acid sites*. J. Phys. Chem. B 103, p. 4611 - 4622.

5. Lukyanov, D. B. *Development of kinetic models for reactions of light hydrocarbons over ZSM-5 catalysts. experimental studies and kinetic modelling of ethene transformation and deactivation of HZSM-5 catalyst, in: Froment, G. F., and Waugh, K. C. (Eds.)*. Reaction kinetics and the development of catalytic process, Stud. Surf. Sci. Catal. 1999; 122: p. 299 - 306.

6. Nguyen, L. H., Vazhnova, T., Kolaczkowski, S. T., and Lukyanov, D. B. *Combined experimental and kinetic modelling studies of the pathways of propane and n-Butane aromatization over H-ZSM-5 catalyst.* Chemical engineering science. 2006; 61: p. 5881 - 5894.

7. Turner, J. *CE30062 Research project report, department of chemical engineering*. University of Bath 2003.

8. Berger, R. J., Stitt, E. H., Marin, G. B., Kapteijn, F., and Moulijn, J. A. *Chemical reaction kinetics in practice.* 2001; cattech 5 (1): p. 30 - 60.

9. Nguyen Huu Luong and Dmitry B. Lukyanov. *Development of a kinetic model for the aromatisation of propane and propene over H-ZSM-5 catalyst under deactivating conditions*. Petrovietnam Journal. 2011; Vol. 6: p. 74 - 78.