Catalysis Letters 13 (1992) 297–304

Catalytic properties of metallosilicates containing iron group metals in light-olefin conversions

Tomoyuki Inui *, Hideo Nagata **, Fumio Okazumi and Hirokazu Matsuda

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakuo-ku, Kyoto 606, Japan

Received 30 September 1991; accepted 12 February 1992

Metallosilicate catalysts containing iron-group metals were prepared by using the rapid crystallization method. These catalysts had the pentasil structure similar to ZSM-5 zeolite. In case of less metal content, the iron-group metal was incorporated into silicate crystal, and contributed to the formation of strong acid sites. The difference in results of light olefin conversion was understood as reflecting the properties of strong acid sites on each metallosilicate.

Keywords: Iron-group metallosilicates; strong acid sites; olefin conversion; olefin oligomers; aromatics

1. Introduction

Different from other conventional zeolites, zeolite ZSM-5 can be synthesized with a very wide range of aluminum content, but less than 1/10 aluminum-to-silicon ratio. Olson et al. [1] emphasized that, in the case of ZSM-5 zeolites, hexane cracking activity was linearly proportional to the aluminum content even in a ppm order concentration. This indicates that if the content of aluminum was varied in the ZSM-5 structure one cannot expect any change in the quality of the catalytic performance, although the degree of reactivity can be changed while maintaining the same catalytic property.

In order to modify the too strong acidic property and hydrogen transfer property of ZSM-5 qualitatively, we have synthesized various kinds of metallosilicates with the pore structure of ZSM-5 [2–4], by substituting the aluminum in

---

* To whom all correspondence should be addressed.

** Present address: Department of Chemical Engineering, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

© J.C. Baltzer A.G. Scientific Publishing Company

ZSM-5 with other transition elements at the stage of gel formation before crystallization.

Even very small contents of the other elements (atomic ratio of silicon to metal $\simeq 3200$) [2,5,6] and a variety of metal sources [7–9] took significant changes in not only the morphology of the crystals formed but also the catalytic performance in methanol conversion, and the results of olefin oligomerization were significantly varied.

The Ga-silicate catalyst converted methanol or light olefins to more aromatic-rich gasoline than the ZSM-5 catalyst [5,6]. The platinum-ion-exchanged Ga-silicate and Zn-silicate catalysts with high metal contents converted light paraffins to aromatic hydrocarbons selectively [10,11]. Fe-silicate catalysts exhibited very high selectivities in methanol-to-olefins conversion [5] and extraordinarily high reaction rate in olefins-to-gasoline conversion [6]. As for methanol conversion, it has been confirmed in our previous study [5] that the catalytic performances of both Co-silicate and Ni-silicate catalysts were similar to that of the Fe-silicate catalyst.

In this paper, the catalytic properties of metallosilicates containing iron-group metals such as iron, cobalt, and nickel in light-olefin conversions were investigated, and moreover, these catalytic properties were compared with that of Al-silicate (e.g. ZSM-5).

2. Experimental

CATALYST

Metallosilicates containing iron-group metals (hereafter, denoted by iron-group metallosilicates) and ZSM-5 were prepared by using the rapid crystallization method [2–4]. As the starting material, the corresponding nitrate salt was used. These metallosilicates were used as the catalysts after protonation. Silicon to metal ratios of these metallosilicates were 3200 and 400. XRD patterns showed that metallosilicates prepared had the same pore structure as ZSM-5.

CHARACTERIZATION OF THE CATALYSTS

The acidity of catalysts was measured by using the technique of temperature-programmed desorption (TPD) of ammonia [12] with Rigaku thermal analyzer TG-DSC-8012. TPD profile was obtained by differential of the integral curve of the weight change. The chemical compositions of the crystals were measured by using a Shimadzu atomic absorption/flame emission spectrophotometer AA-640-01.

REACTION METHOD

An ordinary continuous flow reaction apparatus was used under atmospheric pressure. A 1.0 g (or ca. 1.5 ml) portion of the catalyst was packed in a quartz tubular reactor of 8 mm inner diameter, and pretreated with a nitrogen flow at 500°C for 30 min to standardize the catalyst surface conditions. A reaction gas was fed to the reactor, and produced gas was led to a cooled trap. The integrated formation rate of liquid products was determined by measuring the amount of liquid during a definite time on stream, while the formation rate of gaseous products was determined by measuring the flow rate using a soap film flow meter. The liquid and gaseous products were simultaneously analyzed by using three gas chromatographs equipped with integrators.

The reaction was carried out under the following conditions: reactants; ethylene, propylene, or butenes, reaction temperature; 300°C (for butenes and propylene), or 330°C (for ethylene), space velocity; 1000 h^{-1}, time on stream; 5 h.

3. Results and discussion

ACIDITY OF IRON-GROUP METALLOSILICATES

Ammonia-TPD profiles for the iron-group metallosilicates with silicon to metal ratio 3200 are shown in fig. 1. The profile was composed of two peaks, i.e.

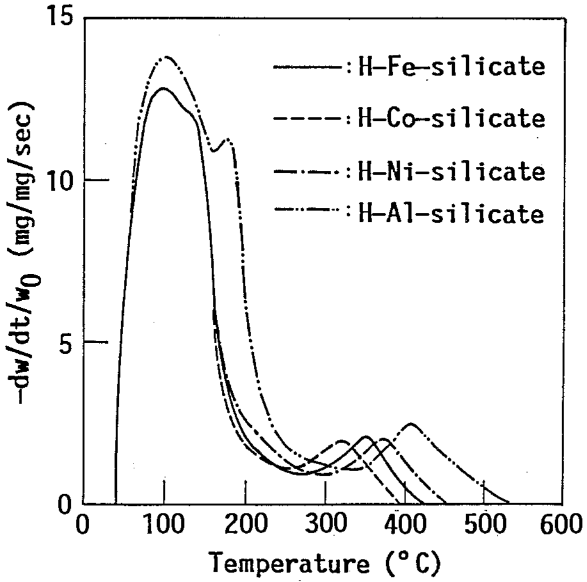

Fig. 1. Ammonia-TPD profiles of iron-group metallosilicates.

Table 1
Results of chemical analyses and amounts of strong acid sites on iron-group metallosilicates

Metal	Charged Si/metal ratio	Observed Si/metal ratio	Amount of strong acid sites (mmol/g-catalyst)
iron	3200	2500	0.19
iron	400	470	0.29
cobalt	3200	3500	0.18
cobalt	400	420	0.27
nickel	3200	3700	0.21
nickel	400	470	0.32
aluminum	3200	1800	0.25
aluminum	400	380	0.46

the high temperature peak of the strong acid sites and the low temperature peak of the weak acid sites [13,14]. The peak temperature is a reflection of the acid strength. In the acid-catalyzed reaction, the strong acid sites play the important role for active sites mainly [13,15]. As shown in fig. 1, the peak temperatures of strong acid sites for Ni-, Fe-, and Co-silicates were 360, 350, and 330°C, respectively while maintaining a roughly same peak area. These temperatures were lower than that for ZSM-5, i.e. 410°C [2]. Therefore, the strength of strong acid sites for iron-group metallosilicates were considered to be lower than that for ZSM-5. Moreover, as for iron-group metallosilicates, the order of the strength of the strong acid sites was as follows:

Ni-silicate > Fe-silicate > Co-silicate.

The results of chemical analysis and amounts of strong acid sites are listed in table 1.

The amount of strong acid sites in the iron-group metallosilicates does not contain the contribution of aluminum impurity.

The observed contents of iron group metal increased with an increase in charged contents, although the amount of the metal incorporated was somewhat lower than that changed except of the case of Fe-silicate of the charged ratio 3200. The observed aluminum contents which came from contamination was suppressed with an increase of the metal incorporation, and therefore, the property of metallosilicate is considered to be caused by the kind of incorporated metal as previously shown [5]. Namely, iron ions were incorporated in silicate crystal, and contribute to the formation of strong acid sites [5]. Analogously, a small amount of cobalt or nickel ions was also incorporated in the silicate crystal and contributed to the formation of strong acid sites.

COMPARISON OF PROPYLENE CONVERSIONS ON IRON-GROUP METALLOSILICATES AND ZSM-5

The distribution of hydrocarbons formed in propylene conversion on ZSM-5 and iron-group metallosilicates with silicon to metal ratio of 3200 is shown in fig. 2. Of all the catalysts, apparent conversions of propylene were higher than 95%. For iron-group metallosilicates, the selectivities of olefins were higher than that for ZSM-5, and moreover, formations of C_1–C_4 paraffins and aromatics were less than that for ZSM-5. Of all the catalysts, the general pattern regarding the order of selectivity of olefins was

Co-silicate > Fe-silicate > Ni-silicate,

and for that of aromatics was increase as follows,

Ni-silicate > Fe-silicate > Co-silicate.

As for even ZSM-5 which produced C_1–C_4 paraffins the best of the four catalysts, the selectivity to CH_4 was 1.0 wt% only. In the case of iron-group metallosilicates, the formation of CH_4 was negligible.

These tendencies also agree with the results obtained in methanol conversion [5]. These results could be explained with the reason of the difference in the strength of strong acid sites. Concerning to light olefins and methanol conversion, the strong acid sites contribute to hydrogen transfer to light olefins [13,15,16] which consequently produces aromatics accompanying the corresponding paraffins.

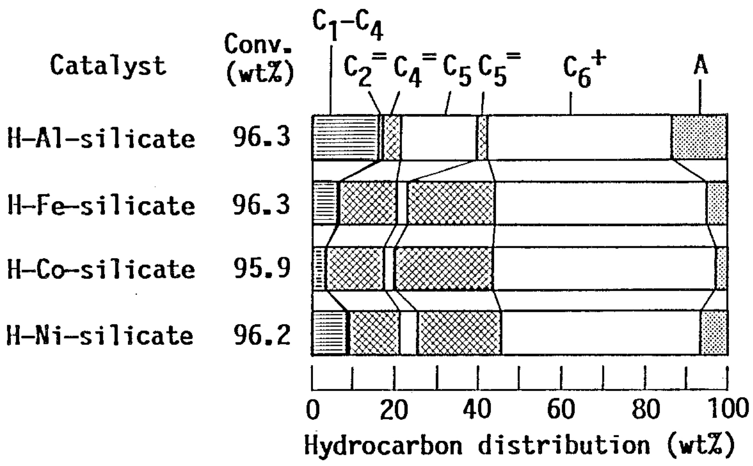

Fig. 2. Hydrocarbon distribution in propylene conversion on iron-group metallosilicates and ZSM-5 with silicon-to-metal ratio of 3200. Reaction temperature; 300°C, GHSV; 1000 h^{-1}, time on stream; 5 h.

Table 2
Selectivities of light olefins and aromatics on iron-group metallosilicates with silicon-to-metal ratios of 3200 and 400

Metal	Charged Si/metal ratio	Selectivity (wt%)	
		Light olefins	Aromatics
iron	3200	35.3	4.94
iron	400	31.9	7.56
cobalt	3200	39.3	3.11
cobalt	400	34.8	4.76
nickel	3200	32.5	6.36
nickel	400	27.5	9.73
aluminum	3200	8.2	13.31
aluminum	400	8.6	18.15

Reaction conditions were the same as in fig. 2.

The tendency of catalytic performances in propylene conversion on all of the catalysts with silicon to metal ratio of 400 were similar to that on all of the catalysts with silicon to metal ratio of 3200.

The selectivities of light olefins and aromatics are listed in table 2. The selectivities of light olefins decreased with an increase in the charged contents of the metals and vice versa for the selectivities of aromatics.

COMPARISON OF ETHYLENE AND BUTENE CONVERSIONS ON IRON-GROUP METALLOSILICATES AND ZSM-5

The distribution of hydrocarbons formed in ethylene conversion on iron-group metallosilicates and ZSM-5 with silicon to metal ratio of 3200 is shown in fig. 3. Differently from the case of propylene conversion, on iron-group metallosilicates, ethylene conversions were apparently low. Especially, on Co-silicate, ethylene conversion was only about 27%. However, the tendency of product distribution of ethylene conversion was consistently similar to that of propylene conversion shown in fig. 2.

The results of 1-butene conversion on iron-group metallosilicates and ZSM-5 having silicon to metal ratio of 3200 are shown in fig. 4.

The apparent 1-butene conversions on all of the catalysts were more than 96%.

However, since the feed 1-butene could not be differentiated from the 1-butene produced by isomerization and/or by cracking in these experiments, it was eliminated from the product distribution shown in fig. 4. Although the introduction of this numerical ambiguity, the general trends of product distribu-

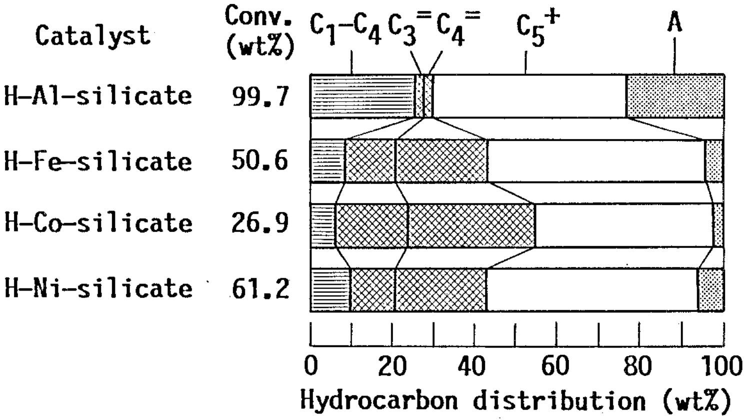

Fig. 3. Hydrocarbon distribution in ethylene conversion on iron-group metallosilicates and ZSM-5 with silicon-to-metal ratio of 3200. Reaction temperature; 330°C, GHSV; 1000 h^{-1}, time on stream; 5 h.

tion consistently coincide with those of propylene conversion and ethylene conversion shown in figs. 2 and 3, respectively. Similar results were also obtained for other butene isomers.

4. Conclusion

The result obtained in this work was a reflection of the strength and/or amount of strong acid sites of each metallosilicate. As for light olefin conver-

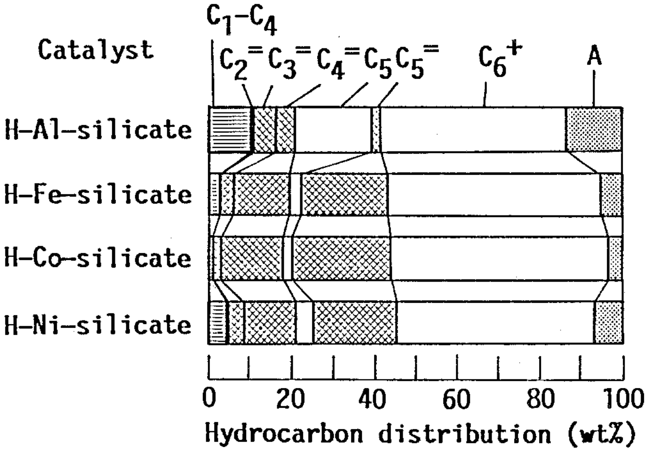

Fig. 4. Hydrocarbon distribution in 1-butene conversion on iron-group metallosilicates and ZSM-5 with silicon-to-metal ratio of 3200. Reaction temperature; 300°C, GHSV; 1000 h^{-1}, time on stream; 5 h.

sion, the strong acid sites are responsible for the aromatization accompanied with the formation of corresponding paraffins. It has been also found that, though a small metal content, cobalt and nickel were incorporated in the silicate crystal as well as iron. They contributed to the formation of strong acid sites which was apparently weaker than that of Al-silicate. Consequently, iron-group metallosilicates exhibit the high selectivity to light olefins while Al-silicate shows the high selectivity to C_1–C_4 paraffins and aromatics.

References

[1] D.H. Olson, W.O. Haag and R.M. Lago, J. Catal. 61 (1980) 390.
[2] T. Inui, O. Yamase, K. Fukuda, A. Itoh, J. Tarumoto, N. Morinaga, T. Hagiwara and Y. Takegami, in: *Proc. 8th Int. Congress on Catalysis*, West Berlin, 1984, Vol. III (Dechema, Frankfurt-am-Main, 1984) p. 569.
[3] T. Inui, Yuki Gosei Kagaku Kyokaishi 44 (1986) 49.
[4] T. Inui, *Zeolite Synthesis*, American Chemical Society Symposium Series, Vol. 398 (American Chemical Society, Washington D.C., 1989) p. 479.
[5] T. Inui, H. Matsuda, O. Yamase, H. Nagata, K. Fukuda, T. Ukawa and A. Miyamoto, J. Catal. 98 (1986) 491.
[6] T. Inui, F. Okazumi, J. Tarumoto, O. Yamase, H. Matsuda, H. Nagata, N. Daito and A. Miyamoto, J. Jpn. Petrol. Inst. 30 (1987) 249.
[7] T. Inui, H. Nagata, O. Yamase, H. Matsuda, T. Kuroda, M. Yoshikawa, T. Takeguchi and A. Miyamoto, Appl. Catal. 24 (1986) 257.
[8] A. Miyamoto, D. Medhanavyn and T. Inui, Appl. Catal. 28 (1986) 89.
[9] T. Inui, H. Nagata, N. Daito, H. Matsuda and A. Miyamoto, Appl. Catal. 51 (1989) 155.
[10] T. Inui, Y. Makino, F. Okazumi, S. Nagano and A. Miyamoto, Ind. Eng. Chem. Res. 26 (1987) 647.
[11] T. Inui, Y. Makino, F. Okazumi and A. Miyamoto, *Innovation in Zeolite Materials Science*, Studies in Surface Science and Catalysis, Vol. 37 (Elsevier, Amsterdam, 1987) p. 487.
[12] T. Inui, H. Matsuda and Y. Takegami, in: *Proc. 6th Int. Zeolite Conf.*, Reno, 1983, eds. D.H. Olson and A. Basio (Butterworths, London, 1984) p. 316.
[13] T. Inui, T. Suzuki, M. Inoue, Y. Murakami and Y. Takegami, *Structure and Reactivity of Modified Zeolites*, Studies in Surface Science and Catalysis, Vol. 18 (Elsevier, Amsterdam, 1984) p. 201.
[14] W.O. Haag, in: *Proc. 6th Int. Zeolite Conf.*, Reno, 1983, eds. D.H. Olson and A. Basio (Butterworths, London, 1984) p. 166.
[15] C.D. Chang and A.J. Silvestri, J. Catal. 47 (1977) 249.
[16] M.L. Poutsma, *Zeolite Chemistry and Catalysis*, American Chemical Society Monograph, Vol. 171 (American Chemical Society, Washington D.C., 1976) p. 680.