Cracking and aromatization properties of some metal modified ZSM-5 catalysts for light alkane conversions

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Abstract

ZSM-5 (HZ) was prepared by hydrothermal synthesis and, zinc and gallium incorporated ZSM-5 catalysts were prepared by adopting incipient wet impregnation (ZnHZ, GaHZ) and co-synthesis methods (Zn-Al-Si and Ga-Al-Si). The acidity and strength distribution of acid sites were measured by micro-calorimetric ammonia adsorption, where Zn-Al-Si and Ga-Al-Si exhibited lower acidity values when compared to the HZ, ZnHZ and GaHZ samples. The *n*-heptane aromatization activity of the catalysts is in the order of Zn-Al-Si > Ga-Al-Si > ZnHZ ~ GaHZ > HZ. The Zn-Al-Si catalyst exhibited the lowest acidity but highest aromatization activity with stable performance in the studied period of 360 min. The catalyst exhibited greater than 80% conversions with 50–65 wt.% selectivity to aromatics for the conversion of various industrial feedstocks namely NGC, light naphtha and raffinate. The major byproduct in this reaction is 21–33 wt.% LPG that makes the catalyst promising for industrial application.
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Keywords: Zn-Al-Si; ZSM-5; NTGG process; LPG; Aromatics; Light naphtha; Raffinate

1. Introduction

Availability of light alkane containing feedstocks such as light naphtha (LN) and natural gas condensate (NGC) demands active and stable catalysts for their conversion into valuable products [1,2]. Such feedstocks contain pentanes and hexanes as major components and cannot be converted in to aromatics by traditional reforming. Moreover, the raffinate obtained after the removal of aromatics from the reformer product itself is rich in pentane and hexane that needs suitable catalytic processes for value addition [3]. Cracking of light alkanes to propane and butane (LPG), isomerization to increase the research octane number (RON) of the feed, and aromatization through dehydrogenation followed by cracking to lower olefins, oligomerization and cyclization are some of the alternative processes for light alkane

conversion [4–6]. Keeping in view the LPG demand in India and other south–east Asian countries, a modified ZSM-5 based catalytic process has been developed for the production of LPG from NGL/LN [7–10]. The process also produces a high-octane gasoline blender as a major byproduct and is named as NTGG (Naphtha/NGL to gas and gasoline). However, the formation of aromatics is limited over H-ZSM-5 catalyst due to the following reasons: (1) thermodynamic data reveal that, in general, alkane-to-aromatics conversion becomes difficult as size of the alkane is decreased, and that aromatics are not thermodynamically favored over the corresponding alkene [11–13]. (2) On H-ZSM-5, the aromatization of alkanes is kinetically limited by the formation of olefinic compounds. This formation occurs through scission of carbonium ions into carbenium ions and hydrogen or alkenes [14]. (3) Formation of aromatics occurs by the hydride transfer from naphthenes to smaller olefins in the final step of the reaction. In this process three moles of smaller paraffins (mainly in the LPG range) formed simultaneously with the one mole of aromatics, which limits the aromatics-to-

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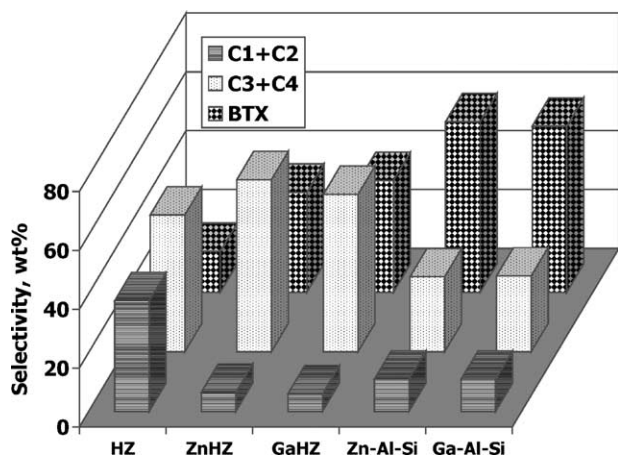 *E-mail address:* nvish@iip.res.in (N. Viswanadham).

Fig. 1. Performance of the HZ and metal loaded HZ catalysts in *n*-heptane cracking and aromatization.

paraffins yield ratio [14], and (4) steric constraints in the pore structure of ZSM-5 limits the hydrogen transfer from naphthenes to olefinic compounds [14] (Fig. 1).

Effective conversion of the paraffins can be achieved by the addition of a dehydrogenating metal to the H-ZSM-5 catalyst [15–17]. The metal ion provides an alternative path for the formation of olefins and aromatics and, controls the formation of lower paraffins from cracking and hydrogen transfer reactions. Aromatization activity of metal-loaded zeolite depends on its hydrogenation–dehydrogenation activity, which ultimately determined by the electronic properties of the metal [18,19]. Inui et al. [20] and Krupina et al. [21] studied the aromatization of propane and *n*-butane, respectively, over various transition metal ion-exchanged ZSM-5 catalysts that underline the superiority of zinc and gallium over the metals studied. Thus, the use of zinc/gallium as a promoter for paraffin aromatization seems logical, however, the activation of lower alkanes by these metal ions is still a point of discussion. Yono and Kanai [22] suggested that Zn/Ga cations are quite effective for the transformation of lower olefins into aromatics, while those cations have no such role in paraffin activation. Mole and Anderson [23] explained the role of zinc as a hydride acceptor in propane activation to produce the propylcarbenium ion. Kanai and Yoneda [24] also reported the role of zinc in the formation of hexene from *n*-hexane over ZnO/H-ZSM-5 catalyst. Studies of Kitagawa et al. [25] supported earlier mentioned ideas on the paraffin activation by zinc as well as by acid sites. That is to say ZnO as well as H-ZSM-5, both take part in the activation of *n*-hexane. Our earlier studies also indicated that Zn provides alternative path of aromatization and suppresses the continuous oligomerization and formation of C_9+ aromatics [26].

Aim of the present study is to understand the activity and stability of zinc/gallium containing H-ZSM-5 catalysts for the conversion of LN, NGC and raffinate, wherein the metal ion is incorporated by different methods. Change in acidic properties of the catalysts due to the incorporation of Zn/Ga was studied by micro-calorimetry. Effect of introduction of

zinc and gallium metal ions into zeolite framework on the activity and stability was studied. In the first phase, performance of various Zn and Ga loaded ZSM-5 catalysts were studied for *n*-heptane conversion where, the Zn-Al-Si prepared by co-addition of Zn at the time of ZSM-5 synthesis exhibited the best aromatization activity. In the second phase of experiments, the studies are concentrated on the Zn-Al-Si catalyst for the conversion of industrial feedstocks.

2. Experimental

2.1. Catalyst preparation

Zeolite ZSM-5 was synthesized using tetrapropyl ammonium bromide as template according to the method of Argauer and Landolt [27]. Detailed procedure has been described elsewhere [26,28]. Similar procedure was adopted for synthesis of Zn and Ga containing ZSM-5 zeolites where, required amount of zinc nitrate or gallium nitrate solutions were added to the initial gel mixture of ZSM-5 to obtain Zn-Al-Si and Ga-Al-Si zeolites, respectively. The gel compositions used for the synthesis of H-ZSM-5, Zn-Al-Si and Ga-Al-Si are given in Table 1. The as-synthesized zeolites were calcined at 773 K for 6 h to destroy the organic template. After calcination, the zeolites were ion-exchanged three times with 1 M ammonium nitrate solution at 373 K for 2 h. After filtration, the zeolites were dried at 393 K over night, and then calcined at 773 K for 4 h to obtain the H-form of zeolite. The samples were denoted as HZ, Zn-Al-Si and Ga-Al-Si, respectively, and the X-ray diffraction (XRD) measurements confirmed that all the samples possess the ZSM-5 structure.

In another method, incipient wet impregnation was used to incorporate Zn and Ga into H-ZSM-5, where the H-ZSM-5 samples were impregnated with $Zn(NO_3)_2$ and $Ga(NO_3)_3$ (Aldrich) solutions, dried at 393 K over night, and then calcined at 773 K for 6 h in air. After this process, zinc and gallium can be converted to ZnO and Ga_2O_3 and the samples are denoted as ZnHZ and GaHZ, respectively.

2.2. Microcalorimetry

The acidity and acid strength distributions of samples were determined on Setaram C-80 (France) heat-flow microcalorimeter attached to a volumetric vacuum adsorption unit for probe molecule delivery. Ammonia was used as a

Table 1
Composition of the zeolite samples

Molar gel composition						Zn or Ga (wt.%)
Catalyst	Si	Al	Zn or Ga	TPA	H_2O	
HZ	0.6	0.03	0.00	0.06	20.0	0.00
Zn-Al-Si	0.6	0.03	0.003	0.06	22.0	1.12
Ga-Al-Si	0.6	0.03	0.003	0.06	23.0	1.20

Measured by XRF.

probe molecule. Prior to adsorption of ammonia, catalyst samples (~0.1 g) were outgassed at 723 K under vacuum and micro-calorimetric measurements of ammonia adsorption have been made at 448 K. Differential heats of ammonia adsorption were determined by introducing small quantities of ammonia (0.02–0.05 mmol/g cat.) on to the outgassed sample, till the neutralization of all acid sites occurred on the catalyst surface. The end of neutralization corresponds to the minimum of differential adsorption heat. The heat of adsorption evolved for each dose was calculated from the resulting thermograms and amount of ammonia adsorbed from the initial and final pressures. Sequential dosing gives the differential heats of ammonia adsorption as a function of coverage.

2.3. Catalyst performance

Performance of the HZ and metal-loaded HZ catalysts were studied using *n*-heptane as a model compound, where the reactant molecule can undergo variety of reactions such as cracking, oligomerization, hydrogen transfer and aromatization reactions. The catalysts were tested in extrudate form and they were prepared by physical mixing of an alumina binder (zeolite:binder = 65:35) followed by the wet extrusion of the mixture. The reaction was conducted in a fixed-bed down-flow reactor made of stainless steel (10 mm dia), at the reaction conditions of 10 kg pressure and 773 K temperature. *n*-Heptane feed was introduced into the reactor containing catalyst bed at 773 K at a flow rate of 20 cm^3/h, which corresponds to a LHSV of 4 h^{-1}. The reactants and products were analyzed by a gas chromatograph fitted with a TCEP column and FID detector. Gaseous products were analyzed using a Squalane column. The conversion and selectivity were calculated based on the carbon number of the components and are defined by the formulae given below:

selectivity (C%) = (products/consumed *n*-heptane) × 100;
yields (%) = conversion × selectivity

A blank test conducted in empty reactor ascertained no reaction occurred under the present reaction conditions.

3. Results and discussion

3.1. Acidity and strength distribution

Micro-calorimetric ammonia adsorption measurements of catalysts are given in Table 2. The acidity was determined by quantity of ammonia adsorbed on a unit weight

of the catalyst. The zeolite sites were classified arbitrarily into strong ($\Delta H NH_3 > 100$ kJ/mol), medium ($\Delta H NH_3 = 100$–75 kJ/mol), and weak ($\Delta H NH_3 < 75$ kJ/mol) acid sites depending upon the heat of adsorption of ammonia evolved on the sites. From the results given in Table 2, it is clear that there is a difference in acidity and strength distribution of the samples. Samples ZnHZ and GaHZ have exhibited higher total as well as strong acidity when compared to the parent H-ZSM-5 (HZ). The initial heat of adsorption was also slightly more on these two catalysts. This may be due to the formation of Lewis acid sites in presence of Zn and Ga in these two catalysts. On the other hand, the co-synthesized metal catalysts Zn-Al-Si and Ga-Al-Si exhibited lower acidity compared to the corresponding H-ZSM-5. However, the strong acidity of these two samples is comparable with HZ, where as weak acid sites are less in Zn-Al-Si and Ga-Al-Si catalysts. Hence, the low value of total acidity of Zn-Al-Si and Ga-Al-Si may be ascribed to the presence of low number of weak acid sites in these samples. From the gel composition given in Table 1, it is clear that the amount of Al present in H-ZSM-5, Zn-Al-Si and Ga-Al-Si are same and the difference is only the presence of Zn and Ga in the framework of Zn-Al-Si and Ga-Al-Si samples. Presence of more weak acid sites in HZ when compared to Zn-Al-Si and Ga-Al-Si may be ascribed to the presence of more hydroxyls groups associated with framework silicon of the former sample.

3.2. Performance in n-heptane conversion

All the five catalysts were tested for their performance in *n*-heptane conversion, where the products obtained were classified into three main groups namely, (1) fuel gas: methane and ethane, (2) LPG: propane and butane, and (3) aromatics: benzene, toluene and xylenes. Here, fuel gas is considered as undesired cracking product, LPG as desired cracking product and BTX as desired aromatics and the classification helps us in catalyst selection for the maximization of LPG or aromatics.

From the data given in Table 3, H-ZSM-5 yields 37.6% fuel gas with 46.5% LPG and 13.9% aromatics, where fuel gas and LPG occupies 82.1 wt.% of the product that is related with the cracking activity of the catalyst. All the metal-loaded catalysts exhibited decreasing fuel gas with simultaneous increase of aromatics (Fig. 1). The highest aromatic yield was

Table 2
Acidity and acid strength distribution

Catalyst	HZ	ZnHZ	GaHZ	Zn-Al-Si	Ga-Al-Si
Acidity (mmol/g cat.)					
Total	1.05	1.14	1.2	0.67	0.88
Strong	0.46	0.56	0.58	0.4	0.52
Medium	0.46	0.44	0.46	0.19	0.26
Weak	0.13	0.14	0.16	0.08	0.1

Table 3
Performance of metal modified ZSM-5 catalysts in *n*-heptane aromatization

Catalyst	HZ	ZnHZ	GaHZ	Zn-Al-Si	Ga-Al-Si
Conversion (%)	90	85	78	68	74.5
Selectivity (wt.%)					
Methane	14.6	4.5	4.2	6.0	6.8
Ethane	23.0	2.0	1.8	5.0	4.1
Propane	38.4	43.4	32.0	10.5	12.0
Butane	8.1	15.1	21.5	15.0	13.8
C$_5$+	2.0	1.0	2.5	5.5	4.8
Aromatics	13.9	34.0	38.0	58.0	56.5

observed with Zn-Al-Si followed by Ga-Al-Si, where as the highest LPG was observed on ZnHZ followed by GaHZ. The better aromatization activity of Zn-Al-Si and Ga-Al-Si may be due to the presence of metals in ZSM-5 framework. These samples also exhibited low values of total and weak acidity. The lower fuel gas and LPG obtained over these catalysts also indicate the suppression of cracking activity, where the alternative pathway through paraffin dehydrogenation facilitated by metal ions may be the reason for lower cracking and higher aromatization activity [20]. Studies of Inui et al. also indicated the better performance of ZSM-5 framework incorporated Zn and Ga catalysts towards propene aromatization [20,29,30]. The performance of the samples were studied for longer periods of 360 min and the product patterns shown in Fig. 2 indicating the superiority of the Zn-Al-Si that exhibited the highest and stable aromatic selectivity among all other catalysts. Though the aromatization activity of Ga-Al-Si is comparable to that of Zn-Al-Si, the former catalysts exhibited relatively lower stability in activity. This may be due to the lower framework stability of Ga compared to Zn. Based on the above mentioned studies, Zn-Al-Si stands as the best catalyst for aromatization reaction and further studies are conducted on this catalyst to see the feasibility of using this catalyst for conversion of other paraffins and industrial feedstocks.

3.3. Effect of reactant chain length

Four paraffins, namely, *n*-pentane, -hexane, -heptane and -octane have been studied on the Zn-Al-Si catalyst at similar reaction conditions. Conversion and product selectivities are shown in Fig. 3. The catalyst exhibited comparable conversions to all the four reactants where as the distribution towards the three major products, namely, fuel gas, LPG and aromatics have been varied. The selectivity to fuel gas does not change much but that of LPG was decreased with simultaneous increase of aromatic selectivity from *n*-pentane to *n*-octane. The results are in agreement with general behavior of H-ZSM-5 reported by Haag et al. [31]. Thermodynamic
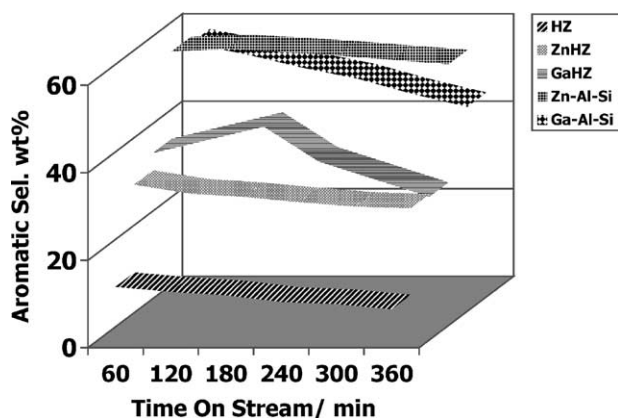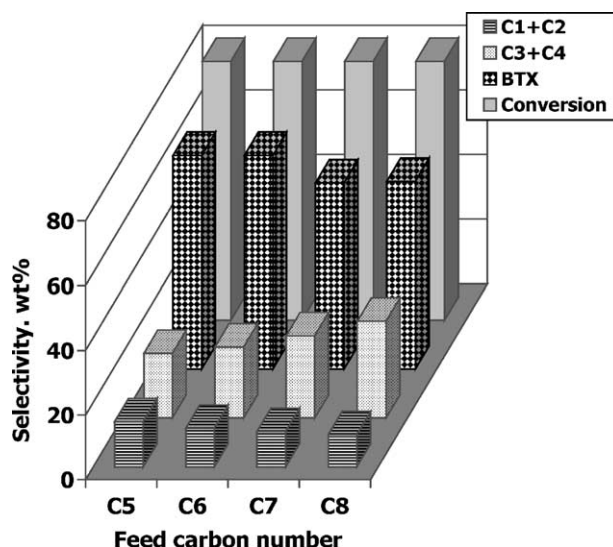
Fig. 3. Effect of carbon number of feed on the conversion and product patterns over Zn-Al-Si.

data also reveal that, in general, alkane-to-aromatics conversion becomes more favorable as the size of the alkane increased, and the aromatics are thermodynamically favored over the corresponding alkane [13]. The higher selectivity of aromatics over *n*-octane can be explained by the higher concentration of olefine fragments formed from this reactant followed by oligomerization, cyclization and aromatization to yield aromatics over Zn-Al-Si. It is important to note that the distribution of aromatics is varied with the carbon number of the feed where, benzene is more with *n*-hexane and toluene is more with *n*-heptane when compared with *n*-pentane and *n*-octane feeds. This observation suggests the possible occurrence of direct dehydrocyclization of paraffins over Zn-Al-Si catalyst. In general, the paraffin aromatization reaction over H-ZSM-5 is considered to occur in a degenerated manner where, irrespective to the initial carbon number of the feed, the intermediates formed are always C_2 to C_4 olefins that oligomerize, cyclize and dehydrogenate to give aromatics eventually. In this case, the selectivity to individual aromatics such as benzene, toluene and xylene is independent to the carbon number of the feed. In order to understand the difference in the reaction mechanism over H-ZSM-5 and Zn-Al-Si, these two catalysts were tested for their performance towards two types of reactants, namely, *n*-paraffins (*n*-hexane and -heptane) and naphthenes (cyclohexane and methyl cyclohexane).

3.4. Effect of hydrocarbon types

From the results given in Table 4, it is clear that the selectivity of aromatics and distribution of BTX are not affected by the nature of the hydrocarbon type over H-ZSM-5. The products obtained with paraffins and naphthenes are comparable. It is interesting to see that the selectivity to toluene is not increased with the C_7 feeds, namely, *n*-heptane and

Fig. 2. Time-on-stream performance of the HZ and metal loaded HZ catalysts in *n*-heptane aromatization.

Table 4
Effect of Hydrocarbon types on the aromatic distribution

Catalyst								
Feed	H-ZSM-5 (HZ)				Zn-Al-Si			
	n-Hexane	*n*-Heptane	Cyclo hexane	Methyl cyclohexane	*n*-Hexane	*n*-Heptane	Cyclo hexane	Methyl cyclohexane
Selectivity to individual aromatics (wt.%)								
Benzene	8	7	6	6	8	7	15	5
Toluene	42	45	43	45	40	45	40	60
Xylenes	50	48	51	49	50	48	45	35

methyl cyclohexane. On the other hand, the performance of Zn-Al-Si indicated the increased selectivities of benzene with n-C_6 and toluene with n-C_7 feed. This indicates the occurrence of direct dehydrocyclization of these n-paraffins over Zn-Al-Si, but not over H-ZSM-5 catalyst. The phenomenon of one step aromatization of hydrocarbons is observed to be more prominent with the naphthene feeds, where the dominance of benzene selectivity from cyclohexane and toluene selectivity from methyl cyclohexane can be seen in the product. These studies indicated that the active sites in Zn-Al-Si are facilitating the one step aromatization of paraffins and naphthenes.

3.5. Studies with industrial feedstocks

In order to study the influence of the interaction of different hydrocarbons present in the commercial feed on the aromatization activity of Zn-Al-Si catalyst, the aromatization reaction was carried out with four industrial feedstocks namely natural gas condensate (NGC), light naphtha-I, -II and raffinate. These feedstocks contain variety of paraffins, isoparaffins and naphthenes. The major component present in all the feedstocks are n-C_5 and i-C_5 that contributes to 55–60 wt.% of the total. Feed characteristics and composition of product obtained over Zn-Al-Si catalyst are given in Table 5. The catalyst exhibited more than 80% conversion with about 50% selectivity to aromatics with all the feedstock, indicating that the catalyst is efficient for the conversion of industrial feeds (mixture of several hydrocarbon types). Among
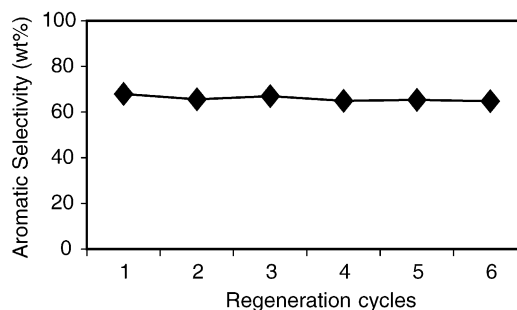

Fig. 4. *n*-Heptane aromatization performance of Pt/Zn-Al-Si with regeneration cycles.

these, the NGC and raffinate feeds have lower IBP and also produced relatively lower aromatics. The highest aromatic selectivity was observed with light naphtha-II (IBP 87–137) followed by light naphtha-I (IBP 70–90). Light naphtha-II feed contains around 10 wt.% of naphthenes and the aromatic selectivity was as high as 63 wt.% with this feed. In addition to this, 21–33 wt.% LPG also formed as a major byproduct with these feedstock. The studies indicated the suitability of Zn-Al-Si catalyst for the production of aromatics with LPG as byproduct from the broad range of industrial feedstock. As can be seen in Fig. 4, the Zn-Al-Si catalyst also exhibited comparable performance even after six regeneration cycles, when 0.3 wt.% of Pt is impregnated on Zn-Al-Si extrudates. Studies are in progress to understand the role of metal ions and their relative contribution to the various reaction steps involved in conversion of light paraffins and naphthenes.

4. Conclusions

Addition of Zn and Ga increased the n-heptane aromatization activity of H-ZSM-5. Among the various methods, the Zn-Al-Si catalyst prepared by co-addition of Zn to the gel mixture at the initial stage of ZSM-5 synthesis exhibited the highest aromatization activity and stability with time-on-stream. Studies conducted on individual hydrocarbon types indicated that the direct aromatization of paraffins and naphthenes were facilitated to an extent on Zn-Al-Si catalyst. The catalyst also exhibited comparable performance in the conversion of various industrial feeds that contain a range of light hydrocarbon components indicating its suitability for industrial applications.

Table 5
Feed characteristics and product selectivities over Zn-Al-Si catalyst

Feed	NGC	Light naphtha		Raffinate
		I	II	
Feed characters				
IBP	35.1	70.0	87.0	46.1
FBP	145.1	90.0	137.0	131.9
Density	0.67	0.72	0.79	0.68
Conversion	85.0	88.0	94.0	91.0
Selectivity (wt.%)				
$C_1 + C_2$	12.0	7.5	8.0	9.5
$C_3 + C_4$	21.0	26.5	22.0	32.5
BTX	52.0	54.0	63.0	49.0
C_5+	12.9	9.2	2.7	6.8
C_9+	2.1	2.8	3.3	2.2

Acknowledgements

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