Research note

The Effects of SiO$_2$ and Al$_2$O$_3$ Binders on the Activity and Selectivity of Bifunctional Fe/HZSM-5 Catalyst in Fischer-Tropsch Synthesis

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Abstract
The influence of SiO$_2$ and Al$_2$O$_3$ binders on the catalyst performance and products selectivity of the precipitated Fe-Cu-K catalyst physically mixtured with HZSM-5 was studied in a fixed bed tubular reactor. The iron catalyst was mixed with HZSM-5 zeolite and shaped to cylinders form by alumina and or silica as a binder for increasing the mechanical strength of bifunctional catalyst. The catalyst activity was tested under reaction condition, P=17 bar, T=290 ^oC , H$_2$/CO=1 and GHSV= 3.07 NL.h^{-1}.g.Fe^{-1}. The results showed that the catalyst activity for Fischer – Tropsch and water gas shift reactions for silica binders is lower than alumina and secondary reactions in the presence of alumina is higher .

Keywords: *Fischer – Tropsch synthesis, HZSM5 Zeolite, Iron Catalysts, Silica binder, Alumina binder, Secondary reaction*

Introduction
Iron catalysts have important applications in carbon monoxide hydrogenation [1-4]. Several factors influence the selectivity and activity of FTS iron catalysts. The effect of various promoters and supports on catalyst performance has been widely investigated [5-8]. Use of shape selective zeolite with iron catalysts for limited hydrocarbon production, particularly gasoline range, is one of the most interesting results of research activities in recent years [9-15]. Physical mixing of iron catalysts and HZSM5, along with an appropriate binder to shape it, makes a catalyst that is able to produce gasoline range (C$_5$-C$_{11}$) hydrocarbons from synthesis gas. These binders have major effects on catalysts activity and selectivity. In this article the influence of binders like silica and alumina has been studied on syngas conversion, products selectivity and octane number of the products.

Experimental
Fe-Cu-K catalyst precursor was prepared by co-precipitation of iron chloride and copper nitrate salt solutions at constant pH and temperature.

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The precipitated powders were washed with deionized water and K_2O and SiO_2 were added to these precursors by impregnation with potassium water glass. The impregnated samples were dried at 120 ^oC for 24h and calcined in air at 450 ^oC. The catalyst composition was designated in terms of the atomic ratio relative to iron (M/ (M+Fe) .100) as: 100Fe/5.64Cu/9.36K/36Si. The iron catalyst was physically mixed with HZSM5 (SiO_2 /Al_2O_3 molar ratio equal to 28) and then alumina or silica in gel form was added as binder and finally shaped to 4mm diameter and 3mm high cylinders by a pelleting press. The catalyst cylinders were dried at 120 ^oC and calcined in air at 450 ^oC.

Catalyst surface area was measured by dynamic nitrogen adsorption in liquid nitrogen using Perkin Elmer gas chromatograph. Temperature–programmed reduction (TPR) experiments were carried out in a fixed-bed quartz reactor. The samples were heated from room temperature to 900^oC at a heating rate of 10^oC/min at 5% H_2/Ar gas flow with space velocity of 18.16 NL.h^{-1}.g-Fe^{-1}. Structural characterization of catalysts was performed by powder X-ray diffraction (XRD) technique on a Philips PW 1840 diffractometer and Cu (K_α) radiation at 40KV and 25 mA. Acidity measurement was conducted by ammonium adsorption/ desorption in a quartz reactor with a temperature increase of 10 ^oC/min from 100 to 500^oC, using frontal chromatography technique.

Catalytic reaction runs were conducted in a fixed-bed stainless steel reactor with an inner-diameter of 2 cm. Gas flow rate was controlled by Brooks electronic mass flow meter and pressure was also controlled by a Brooks compact pressure controller. Four heating zones equipped with a temperature controller and indicator supplied the required reaction heat. 40 g of catalyst was loaded to the reactor then the catalyst was first pre-reduced by using a flow of 5%(v/v) H_2/N_2 and GHSV=15.1NL.h^{-1}.g-Fe^{-1} following a temperature programmed with a temperature increasing rate equal to 5 ^oC/min from ambient temperature to 400^oC and maintained at this temperature for 1 h and then reduced to 270 ^oC. Activation was followed in a stream of synthesis gas with H_2/CO=1 and GHSV= 3.07 NL.h^{-1}.g-Fe^{-1} for 24 h in atmospheric pressure and 270 ^oC. Following reduction, the reactor pressure raised to 17 bar, temperature to 290 ^oC, and reaction started in a stream of synthesis gas with a ratio of H_2/CO=1 and GHSV= 3.07 NL.h^{-1}.g-Fe^{-1}. Online analysis of effluent gases were performed with a TCD detector, two consecutive columns (Propack Q and Molecular sieve), and the switching technique. The liquid phase was detected by an FID detector and separated by a Petrocol Tmdh fused silica capillary column.

Results and Discussion

X-ray powder diffraction patterns for both catalysts are shown in Fig 1. These diffraction data indicate that hematite (Fe_2O_3), HZSM5, Al_2O_3 or SiO_2 phases exist in catalysts. Fig 2 compares the hydrogen consumption during a temperature programmed reduction of catalysts samples containing alumina and silica binders. It has been postulated that the first stage corresponds to the reductions of Fe_2O_3 to Fe_3O_4 and CuO to Cu [16]. The presence of Cu in the catalysts causes the Fe_2O_3 reduction to Fe_3O_4 at a lower temperature because the reduction of CuO, Cu crystallites nucleate and provide H_2 dissociation sites, in turn, leading to reactive hydrogen species capable of reducing Fe oxides at a relatively lower temperature [16]. It is also found that the first stage can be further separated into two peaks; the first peak corresponds to the reduction in the solid solution of CuO, a part of Fe_2O_3 to Cu and Fe_3O_4 [17]. The second stage corresponds to subsequent reductions of Fe_3O_4 to metallic iron. As shown in Fig 2, the area of peaks for an alumina binder are bigger than a silica binder which shows that the catalyst containing alumina binder has

adsorbed more hydrogen and is reduced more strongly. In this case it is expected to show more activity. The effects of binders on catalyst activity, product selectivity, specific surface area and acidity are shown in Table 1.
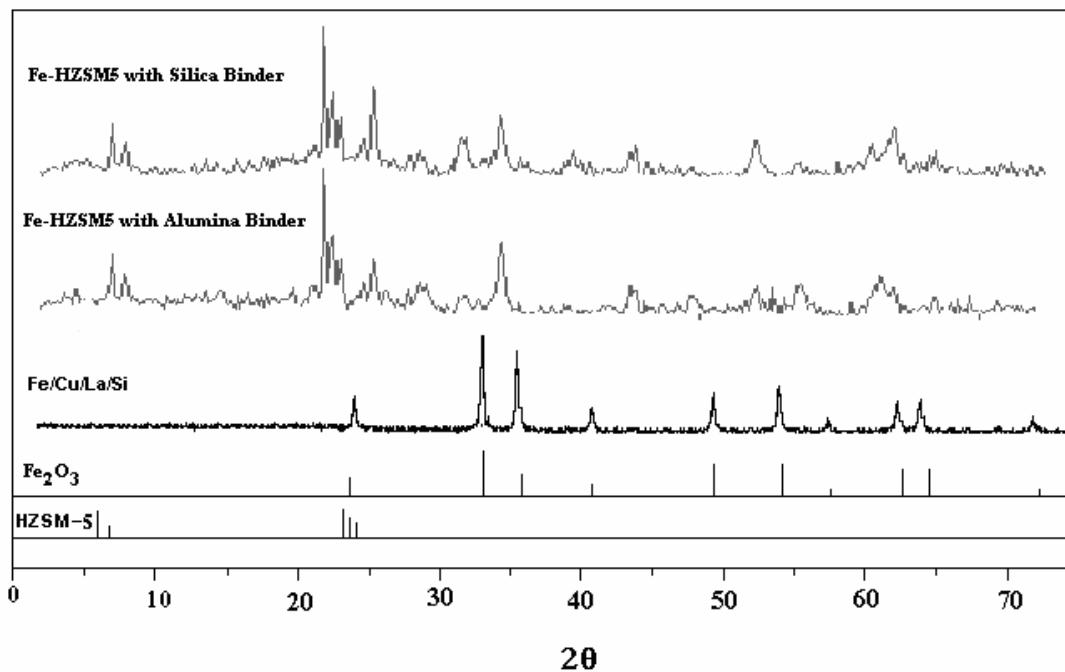
Figure 1. XRD pattern of catalysts
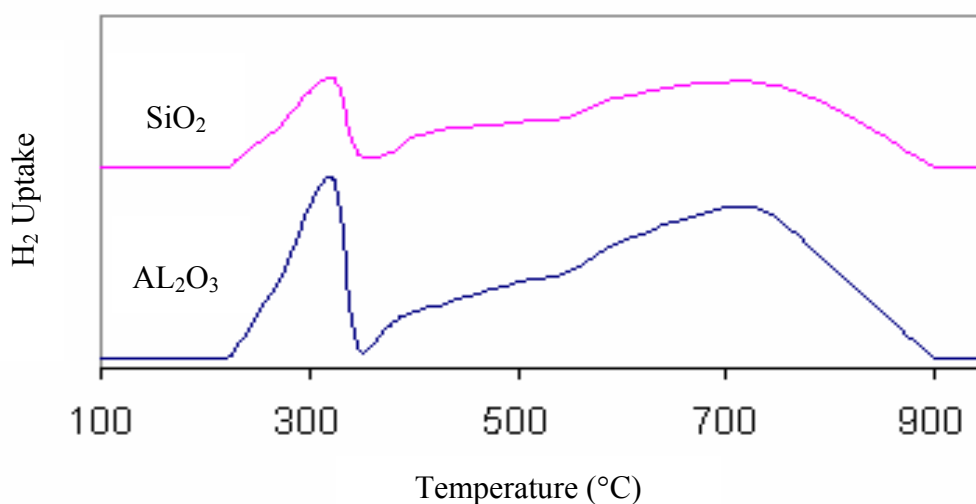
Figure 2. TPR profile of catalysts

Table 1. The effects of binders on catalyst activity, product selectivity, specific surface area and acidity

	Silica Binder	Alumina Binder
Conversion %		
CO	58.14	95
H_2	63.42	82.5
Products Selectivity%		
CO_2	52.20	67.37
H_2O	18.5	6.37
CH_4	4.24	7.6
C_2-C_4	9.59	10.58
C_5+	15.48	8.08
Catalyst area (m^2/g)		
Before reaction	250	270
After reaction	23	26
Catalyst Acidity (mmole NH_3/g.cat)		
Before reaction	0.95	0.99
After reaction	0.52	0.35

Higher CO and H_2 conversion in the presence of alumina binder shows that this catalyst has higher activity than silica binder catalyst, because at a fixed set of process conditions, the CO and H_2 conversion can be used as a measure of FTS activity, i.e. higher conversion implies catalyst activity. Higher activity for alumina catalyst in comparison with silica catalyst may be related to a higher degree of reduction of the first catalyst, shown in Fig 2.

Selectivity of CO_2 for alumina containing catalyst is higher than silica containing catalyst, but the selectivity of H_2O for the silica binder is higher because the WGS activity of alumina binder catalyst is significantly greater than silica binder catalyst where the CO_2 selectivity is used as a measure of the WGS activity [5]. Therefore it is concluded that alumina binder has a greater tendency toward WGS reaction. Reduction in the surface and acidity of catalysts after reaction are due to coke accumulation in the catalyst pores. Table 2 shows the Hy-drocarbon composition in the liquid phase and Research Octane Number (R.O.N.) of products analyzed by gas chromatograph. FTS reaction takes place via absorption of carbon monoxide on the catalysts surface, formation of surface carbide and then chain growth. The chain growth process ends via chain termination [1]. Products segregate from active sites and exit from catalyst pores. But some of the products adsorb on other active sites and cause secondary reactions including olefin hydrogenation to paraffins, isomerization, and cracking [18]. The olefins to paraffin ratio in products is a criterion of secondary reaction participation in the whole reaction process and whenever this ratio increases, the secondary reaction share in the process decreases [19]. Compared to other catalysts iron undergoes less secondary reactions, therefore the amount of produced olefins is higher [1-10]. Incorporation of zeolite in iron catalysts converts the primary products, including olefins and oxygenates, to aromatics and branched hydrocarbons and causes the enhancement of secondary reaction participation in the whole process and, as a result, increases the octane number [9-15]. An enquiry in Table 2 reveals that the ratio of olefins to paraffins for alumina binder catalysts is lower than silica binder catalysts; therefore the participation in secondary reaction for former catalysts is higher. This means that due to occupation of

zeolite pores by silica, its share in the reaction process is lower than alumina containing catalyst. Also, total acidity of the bifunctional catalysts was increased by alumina binder. By increasing the catalyst acidity, the role zeolite in the total reaction was increased. Higher aromatics and branched paraffins, and also a higher octane number for alumina containing catalyst and higher chain paraffins in silica containing catalysts have revealed this. Fig 3 shows the variation of FTS reaction rates and WGS reaction with time on stream. These variations have been calculated from experimentally observed quantities by

$$r_{WGS} = r_{CO_2} \tag{1}$$

and

$$r_{FTS} = r_{CO} - r_{CO_2} \tag{2}$$

Where r_{CO_2} is the rate of CO$_2$ formation and r_{CO} is the rate of CO conversion. The FTS reaction produces water, which is a necessary reactant for the WGS reaction to proceed, thus the rate and extent of the WGS reaction is limited by the amount of water formed by the FTS. Since water is not supplied to the reactor, the stoichiometry of the FTS and WGS reactions (Eqs. [1] and [2]) dictates that [7]:

$$r_{WGS} \leq r_{FTS} \tag{3}$$

Hence, a more reliable measure of the extent of the WGS reaction is how closely the rate of WGS approaches that of the FTS. As it is revealed the rate of FTS and the WGS reaction in the presence of alumina binder is higher than silica. Also, in Fig 3 alumina containing catalyst shows a higher FTS and WGS reaction rate, which confirm its higher activity. Fig 3 shows that at the beginning of the reaction the rates of FTS and WGS reactions for silica containing catalyst is lower and increase as the reaction proceeds, but it is reversed for alumina containing catalyst. It can be concluded that higher reduction, which take place for alumina containing catalysts, caused the difference increment of FTS and WGS reaction rates. But for silica containing catalysts, it suggests that the process of reduction is continued during the reaction, which proves that the activation of silica containing catalyst is lower.
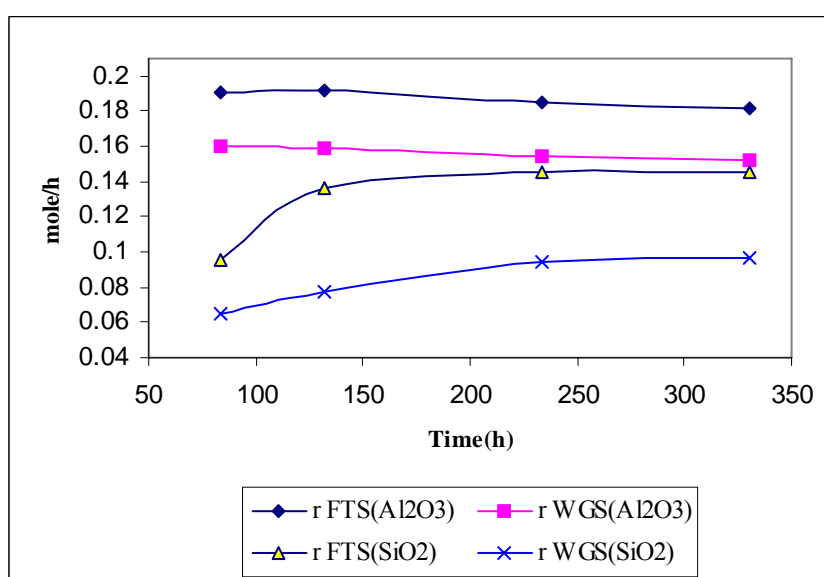

Figure 3. Variation of FTS reaction rates and WGS reaction with time on stream

Table 2. Liquid phase compounds (mol%) and Research Octane Number (R.O.N.) of products analyzed by gas chromatograph

Compounds	Silica Binder	Alumina Binder
Normal Paraffins	29.71	16.93
Iso Paraffins	23.71	33.69
Olefins	18.43	9.86
Aromatics	28.16	39.28
RON	78.93	87.58
Olefins/ Paraffins	0.345	0.195

Conclusion

The influence of SiO_2 and Al_2O_3 binders on the catalyst performance and product selectivity of the percipitated Fe-Cu-K catalyst physically mixtured with HZSM-5 was studied in a fixed bed tubular reactor. The results showed that the catalyst activity for Fischer – Tropsch and water gas shift reactions for silica binders is lower than alumina, because of a higher degree of reduction at a later time. Also, the aromatics content and R.O.N in liquid products, in the presence of alumina is higher, and the olefins to paraffin ratio of the silica binder is higher because of higher secondary reactions in the presence of the alumina binder.

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