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The catalytic performance of different promoted iron catalysts on combined supports Al$_2$O$_3$ for carbon dioxide hydrogenation

Najmeh Bashiri[1] · **Sayed Javid Royaee**[2] ·
Morteza Sohrabi[1]

Abstract Global warming, fossil fuel depletion and fuel price increases have motivated scientists to search for methods for the storage and reduction of the amount of greenhouse gases, especially CO$_2$. The hydrogenation process has been introduced as an emerging method of CO$_2$ capture and convertion into value-added products. In this study, new types of catalysts are introduced for CO$_2$ hydrogenation and are compared based on catalytic activity and product selectivity. The physical properties of the samples are specified using BET. Iron catalysts supported on γ-Al$_2$O$_3$ with different metal promoters ($X =$ Ni, K, Mn, Cu) are prepared through the impregnation method. Moreover, Fe–Ni catalysts supported on HZSM5-Al$_2$O$_3$ and Ce–Al$_2$O$_3$ are synthesized. Samples are reduced by pure H$_2$ and involved in hydrogenation reaction in a fixed bed reactor (H$_2$/CO$_2$ = 3, total pressure = 10 MPa, temperature = 523 K, GHSV = 2000, 1250 nml/min). All catalysts provide high conversion in hydrogenation reactions and the results illustrate that the selectivity of light hydrocarbons is higher than that of methane and CO. It is found that Ni has a promoting effect on the conversion fluctuations throughout the reaction with 66.13% conversion. Using combined supported catalysts leads to enhancing catalytic performance. When Fe–Ni/γ–Al$_2$O$_3$—HZSM5 is utilized, CO$_2$ conversion is 81.66% and the stability of the Fe–Ni catalyst supported on Al$_2$O$_3$ and Ce–Al$_2$O$_3$ furthey improves.

Keywords CO$_2$ hydrogenation · Al$_2$O$_3$ support · Iron catalyst · Hydrocarbon distribution · Nickel catalyst · CO$_2$ Capturing
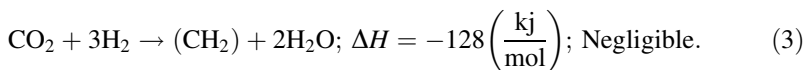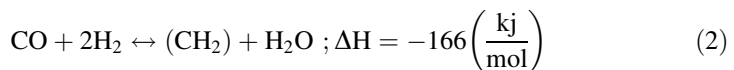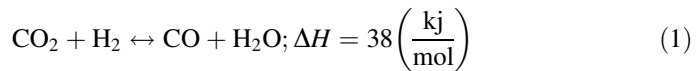

✉ Sayed Javid Royaee
    royaeesj@ripi.ir

[1] Chemical Engineering Department, Amirkabir University of Technology, Tehran, Iran

[2] Petroleum Refining Technology Development Division, Research Institute of Petroleum Industry, Tehran, Iran

Introduction

Global concerns such as earth temperature increase and climate change has put the world under pressure to limit the emissions of greenhouse gases and to find different routes of controlling the amount of them. CO_2 is a greenhouse gas and its amount in the atmosphere has increased rapidly due to the industrial revolution. Therefore, attempts to decrease CO_2 concentrations seem to be necessary. In addition, discharge of fossil fuels and increasing fuel prices have led scientists to study new economical and enironmentally frienly fuels [44–46]. Usage of CO_2 is a strategy that either converts CO_2 into the product or uses it directly in specific applications. The CO_2 conversion process as a source of carbon for value-added products and fuels has been considered as a possible remedy for fossil fuel depletion and the global warming problem [6]. According to the free energy tables, CO_2 is a thermodynamically stable component and it seems that hydrogen with a high energy level can be used as the reagent for CO_2 transformation. It has been claimed that the hydrogenation reaction is one of the most important chemical reactions for converting carbon dioxide [7, 20, 36]. Carbon dioxide can be converted to hydrocarbons by a direct route shown in Eqs. (1)–(3). All heats of reaction are at 300 °C.

$$CO_2 + H_2 \leftrightarrow CO + H_2O; \Delta H = 38\left(\frac{kj}{mol}\right) \tag{1}$$

$$CO + 2H_2 \leftrightarrow (CH_2) + H_2O\ ; \Delta H = -166\left(\frac{kj}{mol}\right) \tag{2}$$

$$CO_2 + 3H_2 \rightarrow (CH_2) + 2H_2O;\ \Delta H = -128\left(\frac{kj}{mol}\right);\ \text{Negligible.} \tag{3}$$

Generally, hydrogenation of CO_2 can be categorized into two main groups according to the final product of the process resulting from various catalysts and operation conditions, such as fuels (hydrocarbons) and chemicals (DME and methanol). Both of these categories have advantages in transport and storage [8, 19, 31, 33]. A thermodynamic analysis has been performed to evaluate the optimal conditions and limitations of CO_2 conversion to methane and methanol from a flue gas exhaust stream. It has been shown that the production of CH_4 is more favorable than methanol from CO_2 hydrogenation considering thermodynamical concepts [32].

Low-temperature catalytic conversion of carbon dioxide into methane has been carried out over Rh/γ–Al_2O_3 catalysts, and 100% selectivity for methane production was achieved [24]. The Co–Cu–ZrO_2 nanomaterial catalyst was synthesized by the reverse co-precipitation method and used for CO_2 hydrogenation. The result showed 58% methane selectivity, 1.27 times higher than the original Co–ZrO_2 catalyst, and 42% CO_2 conversion [43]. There is adequate information for CO_2 hydrogenation to methane but the process is not recommended with respect to oxygenated (methanol, DME), because it includes more consumption of H_2, more difficult storage, and

lower energy production per volume [15]. Thus, synthesis of other kinds of fuels except methane especially as value-added products is indicated.

CO_2 hydrogenation for hydrocarbons production goes through a two-step reaction: reverse water–gas shift (RWGS) and Fischer–Tropsch (FT) synthesis. Catalyst type, operating conditions and types of reactor are the factors that have effects on the process improvement [15]. According to Riedel et al. [38], the calculated equilibrium conversion of the CO_2 hydrogenation reaction was about 72% and actual conversions were between 46 and 53%. Generally, CO_2 conversion and selectivity for C_2–C_5+ have been reported in the range from 19% to 68% and 80%, respectively, in the literature [18, 35, 38, 47]. Fe/Co mixed catalysts have showed low selectivity for the favorable hydrocarbons, with 70 mol% methane production over a Co/Al_2O_3 catalyst in CO_2 hydrogenation [26, 39, 48].

Synthesis of hydrocarbons through carbon dioxide hydrogenation was investigated by Nam et al. [34] using iron supported on alkali metal (Li, Na, K, Rb) ion-exchanged Y-zeolite catalysts in the hydrogenation reaction. The results illustrated that metal exchange in zeolite-Y affects the activity and selectivity of the catalysts by increasing the basicity of the catalyst surface.

CO_2 was converted into iso-alkanes over Fe–Zn–M/Zeolite composite catalysts with different promoters (M=Cr, Mn, Zr, Al, La) in a study by Rongxian et al. [40]. It was found that Zr had a better promoting effect than the other promoters and that the acidity of the zeolite affected the hydrocarbon distribution and catalytic performance.

Satthawong et al. [42] reported that the addition of K promoter over Fe–Co bimetallic Al_2O_3-supported catalysts led to a significant increase in C_2–C_4 olefin formation in CO_2 hydrogenation. They suggested that the result is due to the increasing effect of K on CO_2 adsorption and its decreasing effect on H_2 adsorption on the catalyst surface. Iron is recommended as an active site, and γ-Al_2O_3 and potassium are also suggested as the best support and promoter, respectively, for carbon dioxide hydrogenation via a two-step process [3, 18, 26, 35, 38, 39, 47, 48].

Lee et al. [28] examined the perfomance of CO_2 hydrogenation using K promoter with Fe as an active site in different binders of alumina support. It was reported that alumina Fe-K/γ-$A_{l2}O_3$ (FA-A catalyst) was efficient for CO_2 hydrogenation, while Fe-K/γ-Al_2O_3 (FS A catalyst) dramatically decreased the capability of the process.

Al-Dossary et al. [4] prepared a mesoporous structure catalyst, 0.05 Mn-Fe, using a one-step sol–gel method and used this high specific surface area catalyst in the CO_2 hydrogenation process. The results showed that the catalyst was active in non-oxygenated hydrocarbon production (67.1% C_2–C_6+, C_1 29.3%) and resulted in a small amount of CO production (7.7%).

Selective formation of light olefins of about 53.58% was observed in CO_2 hydrogenation using Fe–Zn–K catalysts prepared via hydrothermal and impregnation procedures. Additionally, catalysts which had uniform particles showed high activity for the CO_2 conversion [4].

Recently, Carlo Giorgio Visconti et al. [43] synthesized a K–Fe catalyst through thermal decomposition and impregnation processes. The catalyst provided high activation in CO_2 hydrogenation into lower olefins at 5 bar. They proposed that

hydrocarbons can be formed from CO produced as a primary component in the RWGS reaction.

Using N-functionalized carbon nanotubes as support in a K–Mn–Fe catalyst resulted in a suitable iron active phase for alkenes production in the CO_2 hydrogenation process [23].

It has been reported that the addition of Mn to iron-based catalysts increases CO_2 conversion and decreases methane formation via its structural and electrical properties [11, 18, 29, 47]. As a promoter, Cu acts naturally as Mn in iron-based CO_2 hydrogenation and leads to increasing the dispersion of the catalyst components [30]. It has been demonstrated that K acts as an electrical promoter in FT and increases the CO_2 canversion by donating electron density to the vacant d orbital of the iron [11–13, 18]. It has been reported that the addition of Ni to iron-based catalysts improves catalytic activity. It can be used as an active promoter in the C–C coupling process during CO hydrogenation under FTS reaction conditions so it can also be suggested for CO_2 hydrogenation [17]. Using ZSM5 in the catalyst structure led to a higher conversion of carbon monoxide and enhanced selectivity shift from methane to higher hydrocarbons based on its ascidic-shape selective characteristic. The researches showed that CO_2 conversion increased with adding Ce to the structure of catalyst. Ce is a WGS catalyst and could be considered as an ideal promoter for iron-based catalysts [16, 37].

In the current work, we have studied the effects of different promoters and combined supports on CO_2 hydrogenation, CO_2 conversion, hydrocarbon distribution, fluctuation of conversion throughout the reaction time and physical properties of samples. The synthesis of Iron catalysts with the promoters Ni, K, Cu and Mn on Al_2O_3 support and also a Fe–Ni catalyst on HZSM5-Al_2O_3 and Ce–Al_2O_3 combined supports were carried out through impregnation, while the combined supports were prepared via some specific techniques. The objective of this work is to recommend effective catalysts for CO_2 hydrogenation.

Experimental

Catalyst preparation

All metals were purchased from Merck. Industrial gamma alumina has a surface area of 128 mm^2/g which was used for the synthesized catalysts. All catalysts were prepared based on the conventional impregnation method by adding aqueous solutions of the metals into specific supports in the nominal composition of 0.35 promoter/1Fe/5 support. The aqueous solutions were composed of $Fe(NO_3)_3 \cdot 6H_2O$ as active metal and one of the $KMnO_4$, K_2CO_3, $Cu(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6-H_2O$ compounds as promoter. In addition, Al_2O_3, Al_2O_3–HZSM5 and Ce-Al_2O_3 were used as different supports. As the first step, Al_2O_3 was entirely dried in a rotary drier for 1 h. The synthesis process of the two other supports and impregnation information is explained in the following sections.

Al_2O_3–Ce support preparation

Alumina and $Ce(NO_3)_3 \cdot 6H_2O$ with 12 Ce/100Al weight ratio were mixing in a flask in the presence of deionized water for 6 h in order to prepare the Al_2O_3–Ce support. Then, the impregnated sample was dried at 100 °C for 12 h. Finally, the sample was calcined at 500 °C in ambient air for 6 h.

Al_2O_3-HZSM5 support preparation

In order to prepare the Al_2O_3–HZSM5 support, aqueous solutions of NaZSM5 and NH_4NO_3 (1 molar solution) were mixed at 40 °C for 4 h. Then, the solution was filtered and the precipitate was dried at 100 °C for 12 h. Subsequently, the dried precipitate was calcined at 500 °C for 6 h. This process was repeated three to five times and HZSM5 was obtained. Thereafter, the HZSM5 and Al_2O_3 in the same weight ratios were combined for 6 h and the impregnated sample dried at 100 °C for 12 h and calcined at 500 °C for 6 h.

Impregnation of the aqueous solution on supports

As the final step for the synthesis of CO_2 hydrogenation catalysts, the aqueous solution of Fe, and one of the promoters were added to the support and were mixed homogeneously for 6 h. Then, the samples were dried at 120 °C for 12 h in ambient air and calcined at 500 °C for 6 h.

Process set up and operating condition

Process of CO_2 hydrogenation was carried out in a catatest set up with a stainless steel fixed bed reactor in bench scale (1.6 cm inner diameter, 70 cm height) surrounded by an electric jacket. A schematic diagram of the process set up is shown in Fig. 1. Prior to the reaction, all catalyst samples were reduced in pure hydrogen for 10 h at the flow rate of 10 nml/min. Temperature and pressure of reduction were fixed at 400 °C and 1 bar, respectively. The reactant gases (H_2 and CO_2) were passed through an MFC (mass flow controller; Booker) at H_2/CO_2: 3/1 ratio. Reactions were carried out at 300 °C and the total flow rates of 1250 and 2000 ml/g-cat at STP condition. In addition, pressure was maintained at 10 bar using a back pressure regulator throughout the reaction. The outlet stream of the reaction was separated in a condenser and the gases were sent to a gas chromatography (Agilent 6890) equipped with HP-plotQ capillary column which uses H_2 and He as internal standard gases. The consumption of the reactants and the production of different hydrocarbons were determined using thermal conductivity and flame ionization detectors (TCD and FID) results.

Characterization test using BET

The Brunauer–Emmett–Teller (BET) method was used to characterize the average pore volume, the mean pore diameter and the specific surface area of the catalyst
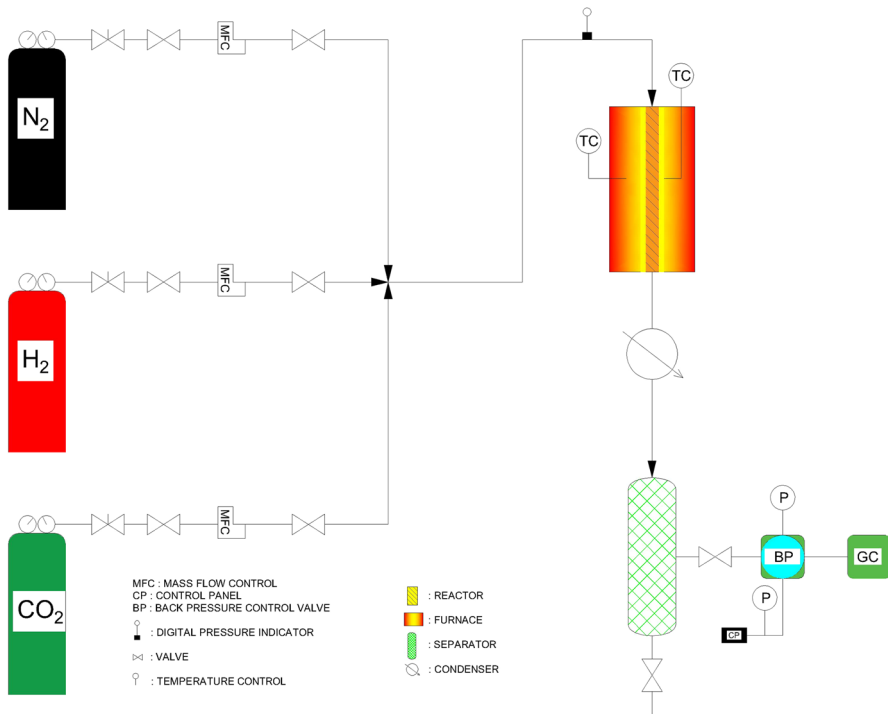
Fig. 1 Schematic diagram of catatest setup

samples. These physical properties were specified by a Quantachrome Autosorb 1 Automated Gas Sorption system (USA), using high-purity N_2 adsorption–desorption isotherm at −196 °C (liquid nitrogen temperature) during 4 h.

Results and discussion

The effects of X promoter on the catalytic performance of Fe-Al₂O₃ supported catalyst

The CO_2 conversion, CO selectivity and hydrocarbons distribution for different catalysts with X=K, Ni, Mn, Cu were calculated at GHSV = 2000 nml/min GHSV = 2000 nml/min and $T = 300$ °C and $P = 10$ bar. The results are illustrated in Table 1. The results showed that CO_2 conversion and hydrocarbons distribution changes by using different promoters, according to their rules [11] The Mn promoter converted CO_2 to products with the conversion of 71.70% and achieved the maximum conversion among other catalyst samples. Then, Ni, K and Cu had the conversions of 66.13, 65.35 and 63.17%, respectively. The samples generally showed a high tendency to form light hydrocarbons. For example, light hydrocarbons selectivity in the distribution of productions is 80.828% when Cu was applied.

Table 1 Catalytic activity Fe–X supported on Al_2O_3 catalysts in CO_2 hydrogenation

Catalyst	% conv. CO_2	% mole CO	% HC	% CH4	% C2–C4	% C2	% C3	% C4	% C5 +
Fe–K/Al_2O_3	65.35	6.730	93.27	13.014	0.558	0.184	0.116	0.258	79.140
Fe–Ni/Al_2O_3	66.13	7.190	92.81	11.167	0.988	0.545	0.382	0.062	79.666
Fe–Mn/Al_2O_3	71.70	8.732	91.268	8.283	2.143	1.330	0.111	0.702	78.699
Fe–Cu/Al_2O_3	63.17	7.704	92.296	9.245	1.11	0.694	0.208	0.211	80.828

CO_2 hydrogenation at $T = 300\ °C$, $P = 10$ atm and GHSV = 2000 ml/gr cat.h

Furthermore, catatestMn promoter produced the highest CO mole percentage among all samples which is 8.732%. K–Fe/Al_2O_3 offered the methane selectivity of 13.014% which is the maximum value for methane production of all samples.

The low methane selectivity is related to the low concentration of the active carbon sites on the catalysts surface due to the CO_2 low dissociation for acidic catalysts [43]. The increment of iron oxide concentration decreases the acidity of the catalysts surface leading to the reduction in methane selectivity.

The fluctuations of CO_2 conversion throughout the reaction for different samples are shown in Fig. 2. When the promoter is Cu, the range of conversion fluctuations is the widest among all samples and there is a huge reduction in the amount of conversion during the reaction time. According to the results, Mn and Ni presented more stability in conversion throughout the reaction.

It has been reported that Mn acts as both a structural and electronic promoter. Applying the Mn promoter on the iron catalyst causes methane formation
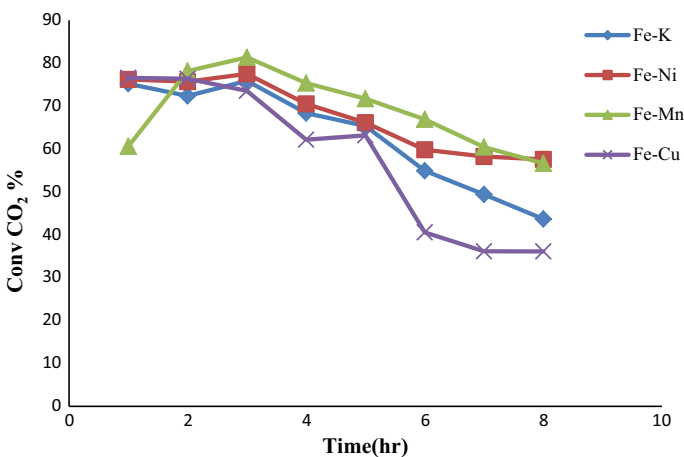

Fig. 2 The fluctuation of CO_2 throughout the hydrogenation reaction for different promoted catalysts ($T = 300\ °C$, $P = 10$ bar, $H_2/CO_2 = 3/1$ and GHSV = 2000 ml/gr cat.h)

suppressing [1, 11, 18]. It is proposed that the Mn promoter raises the basicity of the catalyst's surface. Using Mn has been reported to augment the reduction of the catalyst as well as the carburization and dispersion of Fe_2O_3-state being advanced by using Mn. The basicity of the catalyst surface is suppressed possibly by incorporating of the promoter into the iron lattice [29, 41]. Although Mn promotes catalyst activity in some aspects like increasing conversion, it leads to blocking the active sites of catalyst and decreasing CO conversion to hydrocarbons, which is the second step in CO_2 hydrogenation [12, 29]. So, promoters other than Mn like Cu, Ni, K are preferred for the hydrogenation process.

It has been reported that the addition of Cu as a reducing metal raises the activity of the Fe catalyst and enhances the dispersion of the catalyst particles [5, 30]. It has been suggested that Cu promotes the reduction of the hematite particles during carburization. Active sites for the dissociability of the adsorbing hydrogen are created with reducing of the copper to its metallic form [18]. The metallic form of Cu supplies active sites for adsorbing dissociated hydrogen [41]. The copper performance is comparable with the Mn promoting performance in nature. According to the results, Cu showed more CO_2 conversion and less fluctuations than the other promoters, so Ni and K are preferred as promoters.

It has been demonstrated that the electronic role of potassium in the FT process is more than its structural role, but generally the role of K promoter in CO_2 hydrogenation and FT is not obviously specified [14, 41]. Adding the K promoter significantly affects the overall performance and also increases the CO_2 conversion [9, 12, 25, 27]. It has been observed that the addition of K enhances the alkene/alkane ratio and shifts the products distribution to longer-chain hydrocarbons [12]. It has been demonstrated that K lowers the work function of metal via donating electron density to the iron d orbital, decreasing the H_2 adsorption ability and increasing the adsorption of CO which results in the reduction in the hydrogenation of alkenes [11, 14]. Using K has been reported as a factor for increasing CO_2 conversion [9, 27].

Nickel-based catalyst performance exhibits high CO_2 conversion and offers more CH_4 selectivity for the hydrogenation process [2, 21].

The effects of support on the performance of Fe–Ni catalyst

Table 2 shows the comparison between Fe–Ni catalysts on HAZM5-Al_2O_3 and Al_2O_3 supports in terms of CO_2 conversion, CO selectivity and hydrocarbon

Table 2 Catalytic activity Fe–Ni supported on Al_2O_3 and Al_2O_3-HZSM5 catalysts in CO_2 hydrogenation[a]

Catalyst	% conv. CO_2	% mole CO	HC%	% $CH4$	% C2– C4	% C2	% C3	%C4	C5+
Fe–Ni/Al_2O_3	66.13	7.190	92.810	11.167	0.988	0.545	0.382	0.062	79.666
Fe–Ni/ HZSM5·Al_2O_3	81.66	9.302	90.598	18.620	0.263	0.187	0.021	0.055	71.815

CO_2 hydrogenation at $T = 300$ °C, $P = 10$ atm and GHSV = 2000 ml/gr cat.h

distribution at GHSV = 2000 nml/min. Table 3 also illustrates the comparison between Fe–Ni catalysts on Ce–Al_2O_3 and Al_2O_3 supports based on the aforementioned parameters at GHSV = 1250 nml/min. According to the results, adding HZSM5 to Al_2O_3 increases CO_2 conversion by 15.53% and enhances the composition of methane in the product. The conversion difference between Ce-Al_2O_3 and Al_2O_3 supports at GHSV = 1250 nml/min is not significant. However, methane selectivity by using Ce was three times less than a simple support. It has been demonstrated that decreasing GHSV from 2000 to 1250 nml/min results in the increment of conversion and methane selectivity. Figure 3 shows the fluctuations of CO_2 conversion throughout the reaction for combined supports and Al_2O_3. As the figure indicates, the conversion changes are diminished by using combined supports. It is suggested that HZSM5 can have both a support role and a catalyitic role due to its high surface area and well-defined structure. Therefore, the conversion and the stability of catalyst increases by adding HZSM5 to the support [10, 22].

Ceria can be utilized on iron-based catalysts for WGS and RWGS reactions. It has beenis reported that using ceria and iron leads to large amounts of CO production from CO_2. However, it has been shown that it prevents chain growth due to the active sites blocking of iron and deactivates the catalyst in the hydrogenation process [13, 16, 37]. According to these studies, HZSM5 is suggested as an added support to Al_2O_3 because it improves the conversion and stability of the catalyst throughout the reaction time.

Characterization of iron based catalysts

According to N_2 adsorption–desorption isothermal diagrams, it can be concluded that the mesoporous structure of alumina is retained in all samples and that the impregnation process has no specific effect on the structure. Pore size of samples ranges from 57 to 60 nm and pore size distribution diagrams are similar. Specific surface area, average pore diameter and average pore volume for samples are summarized in Table 4. It is proposed that specific surface area for the metals on Al_2O_3 is directly related to the conversion and the values of specific surface area were obtained as 206.8, 205.8, 173.4 and 165.3 m^2/g respectively in the presence of Mn, Ni, K and Cu promoters. Although catalysts with combined support Ce–Al_2O_3 offered maximum specific surface of about 347.2 m^2/g, its catalytic performance was not the highest. The specific surface area of Fe–Ni/HZSM5–Al_2O_3 was low

Table 3 Catalytic activity Fe–Ni supported on Al_2O_3 and Al_2O_3–HZSM5 catalysts in CO_2 hydrogenation

Catalyst	% conv. CO_2	% mole CO	HC%	% CH4	% C2–C4	% C2	% C3	%C4	C5+
Fe–Ni/Al_2O_3	100.00	9.600	90.399	24.840	0.559	0.426	0.120	0.011	65.000
Fe–Ni/ HZSM5·Al_2O_3	98.39	11.569	88.431	8.616	0.245	0.207	0.033	0.005	79.570

CO_2 hydrogenation at T = 300 °C, P = 10 atm and GHSV = 1250 ml/gr cat.h

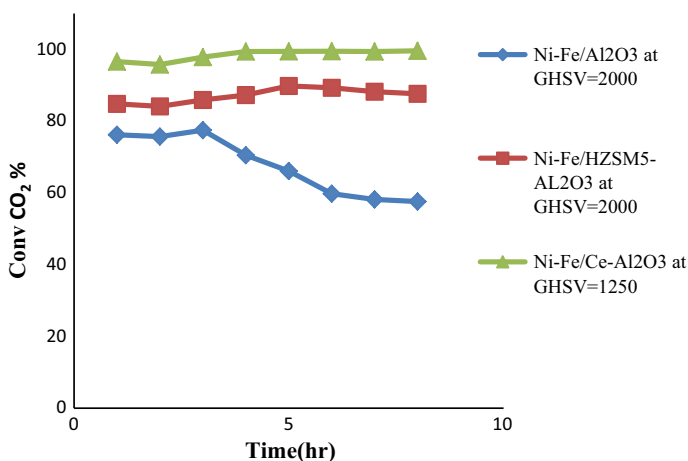**Fig. 3** The fluctuations of CO_2 conversion throughout the hydrogenation reaction for Fe–Ni catalysts on different supports ($T = 300\ °C$, $P = 10$ atm, $H_2/CO_2 = 3/1$ and GHSV $= 2000$ ml/gr cat.h)

Table 4 Structural properties of different iron-based catalysts	Sample	s_{BET} (m²/g)	d_A(cc/g)	V_A(cc/g)
	Fe–K/Al$_2$O$_3$	173.4	19.71	0.0854
	Fe–Ni/Al$_2$O$_3$	205.8	19.22	0.0989
	Fe–Mn/Al$_2$O$_3$	206.8	19.27	0.0996
	Fe–Cu/Al$_2$O$_3$	165.3	19.61	0.0811
$sBET$ specific surface area, d_A average pore diameter, V_A average pore volume	Fe–Ni/Ce·Al$_2$O$_3$	347.2	19.40	0.0168
	Fe–Ni/HZSM5·Al$_2$O$_3$	166.5	19.08	0.0794

compared to other samples (166.5 m²/g); however, it provided high conversion and stability. Therefore, it is suggested that the catalytic activity for Fe–Ni/HZSM5–Al$_2$O$_3$ was useful.

Conclusion

An iron catalyst promoted by Ni, K, Mn, Cu on γ-alumina support was prepared and the catalytic activity of these samples were compared in the operating conditions. It was found that Ni showed a promoting effect on the conversion fluctuations throughout the reaction having the conversion of 66.13%. The catalytic performance of the Fe–Ni catalyst on HZSM5–Al$_2$O$_3$ and Ce–Al$_2$O$_3$ combined supports was studied. The results illustrated that HZSM5-Al$_2$O$_3$ increases CO_2 conversion up to 81.66%. In addition, light hydrocarbons were the main product in the CO_2 hydrogenation of all the catalyst samples. Moreover, methane production and CO_2 conversion were increased with decreasing GHSV from 2000 to 1250 nml/min.

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