Hydrogenation of carbon dioxide over Fe–Cu–Na/zeolite composite catalysts: Na migration via solid–solid reaction and its effects on the catalytic activity

Qiang Xu [*], Dehua He [1], Masahiro Fujiwara, Mutsuo Tanaka, Yoshie Souma, Hiroshi Yamanaka

Osaka National Research Institute, AIST, MITI, 1-8-31 Midorigaoka, Ikeda, Osaka 563, Japan

Abstract

Composite catalysts containing zeolites and Na-rich Fe–Cu Fischer–Tropsch catalysts were studied for the hydrogenation of carbon dioxide at 250°C. Sodium migration from the surface of the F–T catalyst to the zeolite via solid–solid reaction seemed to change the acidity of the zeolite and the reduction degree of the Fe catalyst, which finding was supported by TG and XRD measurements. It was shown that branched and higher hydrocarbons can be obtained in good yields by using composite catalysts containing iron-based catalysts with moderate alkali content and zeolites with suitable acidity. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Carbon dioxide; Hydrogenation; Composite catalysts; Iron; Copper; Sodium; Zeolites; Thermogravimetric analysis; Reduction; Solid–solid reaction

1. Introduction

Hydrogenation of carbon dioxide is important for its utilization as a carbon resource [1]. Iron-based catalysts, which were originally used in the Fischer–Tropsch (F–T) synthesis, have been used for the hydrogenation of carbon dioxide to hydrocarbons [2–9]. It is well known that the addition of a reducible metal such as Cu enhances the catalytic activity of Fe catalysts [10–16]. On the other hand, alkali addition is known to reduce the extent of secondary hydrogenation of primary α-olefin products in the F–T synthesis based on Fe, leading to high olefin selectivity [2,6,14,15]. In the F–T reaction, the major products are linear hydrocarbons, which have a distribution that is limited by the Anderson–Schulz–Flory (ASF) polymerization kinetics, while the branched and liquid hydrocarbons are the more commercially valuable products [10–12].

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[*] Corresponding author.
[1] Present address: Department of Chemistry, Tsinghua University, Beijing, China.

Composite catalysts containing two different components have recently been used to improve the distribution of products [17–26], and have been studied using two different approaches. One combines the methanol synthesis and the methanol to gasoline (MTG) reaction [17–23] and the other approach is the combination of the F–T reaction and the reforming reaction of hydrocarbons [24–26]. It was recently shown that zeolites can change the function of F–T catalysts, as demonstrated by Fe–ZnO/HY [18]. Fe–ZnO/HY behaves as a composite catalyst combining the methanol synthesis and the MTG reaction, although the F–T reaction is catalyzed by Fe–ZnO. It seems that the catalytic site for the F–T reaction based on Fe catalysts is preferentially deactivated by the coexistent HY zeolite, which probably originates from the acidic sites of the zeolite.

By combining the F–T catalyst and the zeolite, branched hydrocarbons might form via the acidic carbon-homologation of primary olefin products on zeolite. Fe–Cu–Na/zeolite is therefore expected to be useful for obtaining branched products. We wish to report here that physical mixing of zeolites with Fe–Cu–Na catalysts improves the catalytic activity and enhances the generation of branched and higher hydrocarbons in the hydrogenation of carbon dioxide. A preliminary account of the Fe–Cu–Na/zeolite composite catalysts has been reported recently and introduced the idea of Na-migration to explain the change of catalytic activity [27]. In the present paper, we describe the catalytic properties of the composite catalysts in detail and report TG studies on the reduction behavior of the catalysts, which is modulated by Na migration and influences the catalytic performance.

2. Experimental

The Fe–Cu–Na catalysts were prepared by coprecipitation from a solution containing iron and copper nitrates with sodium hydroxide. Sodium content was controlled by washing the precipitates. The precipitates were dried at 110°C for 6 h and calcined at 400°C for 4 h in air. The Na contents were determined by atomic absorption spectrometry and the Fe and Cu contents by inductively coupled plasma spectrometry. The composite catalysts were obtained by physical mixing of equal amounts of Fe–Cu–Na oxides and zeolites. Use was made of the zeolites of HY(4.8), HMOR(9.8), US-Y(10.7), HZSM-5(25), HZSM-5(1000) and NaY(4.8) (the reference catalysts of the Catalysis Society of Japan; ratio, SiO_2/Al_2O_3, in parentheses). For the sake of comparison, silica and silica–alumina were also employed. After reducing the samples in a flow of H_2 diluted with N_2 (10% H_2/N_2, 3000 ml g^{-1} h^{-1}) for 6 h at 350°C, the catalysts were kept at 250°C in a flow of reaction gas ($H_2/CO_2 = 3$, SV = 3000 ml g^{-1} h^{-1}) under 20 atm. The reactants and products were analyzed with an on-line gas chromatograph system, which was composed of three gas chromatographs; one with Porapak Q (1.6 m) for carbon dioxide and ethane and molecular sieve 13X (4 m) for methane and carbon monoxide, one with a capillary column (Chrompack PLOT-Al_2O_3/KCl, 50 m) for hydrocarbons (C_1 to C_8), and the other with BX-10 (5 m) for alcohols (C_1 to C_3).

Reduction performance of the same catalysts as used in the hydrogenation reaction were examined on a thermogravimetric analyzer (SEIKO TG-DTA320U). The weight of sample used for the analysis was either 10 mg for the iron-based catalysts, or 20 mg for the composite catalysts (containing an equal amount of the Fe catalyst and the physically mixed zeolite). The catalysts were heated from room temperature to 250°C for 30 min and kept at 250°C for 2 h in a flow of Ar gas (100 ml/min, 1 atm), which lost weight with desorbing water and reached equilibrium during the pretreatment. The weight loss was then recorded against reduction time with the catalysts kept in a constant flow of 5% H_2/Ar (100 ml/min, 1 atm) at the constant temperature of 250°C.

3. Results and discussion

3.1. The effect of addition of Na on the catalytic activity of the Fe–Cu catalyst used for the hydrogenation of carbon dioxide

Table 1 shows the results of hydrogenation of carbon dioxide over Fe–Cu (99:1 in molar ratio) catalysts with various Na contents at 250°C. The distribution of hydrocarbons in the products follows the Anderson–Schulz–Flory law [10–12]. The variations induced by the Na addition to the iron catalyst include (1) an increase in the average molecular weight of hydrocarbon products (i.e., decrease in the production of methane and light hydrocarbons), (2) an increase in olefin selectivity, (3) an increase in activity for the reverse water gas shift (RWGS) reaction (i.e. an increase of CO selectivity), and (4) an increase in F–T activity (i.e. an increase in hydrocarbon yield) at low alkali concentrations (**C2**), followed by a decrease at higher levels of Na addition (**C3** and **C4**).

The results are consistent with the previous reports on the effect of alkali promotion on iron catalysts for F–T synthesis [14–16,28,29]. Low F–T activity at high levels of alkali promotion has also been observed in the hydrogenation of carbon monoxide over iron-based catalysts [14]. Alkali doping has been generally interpreted in terms of electronic effects [16,30]: the electron-donating alkali additive transfers electrons to the metallic phase, thus strengthening the bonds between the metals and electron-acceptor molecules such as CO, N_2 and weakening the bonds between the metals and electron-donor elements such as hydrogen. The present observation of low catalytic activity for the hydrogenation of CO_2 at high levels of Na promotion (**C3** and **C4**) is therefore attributable to the weakening of the iron–hydrogen bond, in other words, the lowering of the degree of reduction. The inhibitory effect on reduction through addition of alkali has been demonstrated by investigating the reduction behavior of iron based F–T catalysts using thermogravimetric and differential thermometric analysis (TG–DTA) [31].

As shown in Table 1, Na-poor catalysts exhibit high CO_2 conversion with low selectivity to olefins and low average molecular weight of hydrocarbons. On the other hand, Na-rich catalysts give a product with a high average molecular weight and high olefin content, but low CO_2 conversion. Both the Na-rich and Na-poor catalysts give only minor amounts of the more desirable branched hydrocarbons [10–12]. Since branched hydrocarbons can form via the acidic carbon-homologation of primary olefin products on zeolite, physical mixing of Na-containing iron-based catalysts with zeolites might be expected to improve the selectivity of product formation.

Table 1
The variation in activity of the Fe–Cu catalyst upon addition of Na[a]

Cat. no.	Catalyst[b]	Conversion of CO_2 (%)	Convert to (C-mol %)					$C_=$ ratio[d]	C_{brch} ratio[e]
			CO	C_1	C_2–C_4	C_{5+}	Oxy[c]		
C1	Fe–Cu–Na (99:1:0.06)	13.8	20.8	26.5	35.7	11.8	5.2	2.9	7.2
C2	Fe–Cu–Na (99:1:0.17)	14.4	19.5	27.6	36.4	12.0	4.5	3.2	6.2
C3	Fe–Cu–Na (99:1:1.45)	6.8	69.0	4.7	14.4	9.0	2.9	70.5	2.9
C4	Fe–Cu–Na (99:1:27.0)	6.7	71.9	4.7	13.8	7.4	2.1	64.5	3.3

[a] 250°C, 20 atm, SV = 3000 ml (g catalyst)$^{-1}$ h^{-1}, $H_2/CO_2 = 3$. Results after 5 h.
[b] Molar ratio in parentheses.
[c] MeOH + EtOH + PrOH.
[d] Olefin/(olefin + paraffin) % of C_2, C_3 and C_4.
[e] Branched/(branched + linear) % of C_4, C_5, and C_6.

3.2. The effect of physical mixing of Fe–Cu–Na catalysts with zeolites on the catalytic activity

3.2.1. The catalytic activity of a Na-poor Fe–Cu catalyst physically mixed with zeolites

We first examined composite catalysts composed of the Na-poor catalysts of Fe–Cu–Na (99:1:0.06) physically mixed with zeolites, for which Na has a negligible influence (Table 2). Physical mixing with the HY zeolite (**C5**) decreased the conversion of CO_2, and produced less C_{5+} hydrocarbons. H-type zeolites with the higher Si/Al ratios, which have fewer acidic sites (**C6**–**C9**), and the Na-type zeolites, which have no acidic sites (**C10**), almost did not deactivate the F–T catalytic activity. This indicates that the acidic sites are closely related to the deactivation process. Since the activity of the catalysts was not reduced during the reaction, coke-formation can be excluded and it is concluded that the catalysts were deactivated during the pretreatment. The previous work on the composite catalyst of Fe–ZnO/HY also revealed that the catalytic sites required for the F–T reaction seemed to be preferentially deactivated by the acidic sites of coexistent HY zeolite, while the catalytic activity of Fe–ZnO for

methanol synthesis was still effective, enabling hydrocarbon formation via MTG reaction [18].

Physical mixing of the Na-type zeolite with the iron-based F–T catalyst (**C10**) did not change the selectivity of olefins and branched hydrocarbons. On the other hand, physical mixing of H-type zeolites (**C5**–C9) produced a product containing less olefins and more branched hydrocarbons, which therefore appears to be formed via the acidic carbon-homologation of primary olefin products on the acidic sites of zeolites. Small amounts of higher weight hydrocarbons (C_{5+}) appeared for both of the Na-poor Fe–Cu catalyst and its composite catalysts.

3.2.2. The catalytic activity of Na-rich Fe–Cu catalyst physically mixed with zeolites

Table 3 summarizes the results of the hydrogenation of carbon dioxide over the Na-rich Fe–Cu catalyst of Fe–Cu–Na (99:1:1.45) and its composite catalysts. Physical mixing of zeolites with the catalyst **C3** led to an increase of CO_2 conversion (6.8 (**C3**) → 11.8 (**C13**), 11.5 (**C14**), 12.3 (**C15**) and 12.3 (**C18**) C-mol %) and improved yields of hydrocarbons, although the zeolite itself does not possess F–T activity or the ability to directly promote the reduction

Table 2

Hydrogenation of carbon dioxide over the Na-poor catalyst of Fe–Cu–Na (99:1:0.06) physically mixed with zeolites[a]

Cat. no.	Zeolite[b,c]	Conversion of CO_2 (%)	Convert to (C-mol %)					$C_=$ ratio[e]	C_{brch} ratio[f]
			CO	C_1	C_2–C_4	C_{5+}	Oxy[d]		
C1	–	13.8	20.8	26.5	35.7	11.8	5.2	2.9	7.2
C5	HY(4.8)	8.4	25.5	33.5	36.0	5.1	0	0.6	61.5
C6	HMOR(9.8)	13.0	13.5	34.7	41.1	8.9	1.8	1.7	43.4
C7	US-Y(10.7)	12.5	14.8	35.1	41.4	8.7	0	0.5	76.4
C8	HZSM-5(25)	13.6	17.1	33.3	35.6	13.3	0.6	0.6	72.6
C9	HZSM-5(1000)	13.1	18.5	34.1	36.7	8.4	2.3	1.2	28.8
C10	NaY(4.8)	12.8	15.1	34.7	35.9	8.2	6.2	2.2	6.3

[a] 250°C, 20 atm, SV = 3000 ml (g cat.)$^{-1}$ h^{-1}, H_2/CO_2 = 3. Results after 5 h.
[b] Reference catalysts of the Catalysis Society of Japan; equal amounts of metal catalyst and zeolite physically mixed.
[c] Ratio, SiO_2/Al_2O_3, in parentheses.
[d] MeOH + EtOH + PrOH.
[e] Olefin /(olefin + paraffin) % of C_2, C_3 and C_4.
[f] Branched/(branched + linear) % of C_4, C_5, and C_6.

Table 3
Hydrogenation of carbon dioxide over the Na-rich catalyst of Fe–Cu–Na (99:1:1.45) physically mixed with zeolites[a]

Cat. no.	Zeolite[b,c]	Conversion of CO_2 (%)	Convert to (C-mol %)					$C_=$ ratio[f]	C_{brch} ratio[g]
			CO	C_1	C_2–C_4	C_{5+}	Oxy[e]		
C3	–	6.8	69.0	4.7	14.4	9.0	2.9	70.5	2.9
C11	SiO_2–Al_2O_3(4.2)[d]	8.1	33.4	18.9	25.1	15.0	7.8	17.6	4.6
C12	HY(4.8)	8.2	33.4	21.3	32.5	12.8	0	1.1	69.6
C13	HMOR(9.8)	11.8	23.7	17.6	36.6	21.8	0.3	15.7	44.0
C14	US-Y(10.7)	11.5	22.7	24.0	36.3	17.0	0	0.3	77.3
C15	HZSM-5(25)	12.3	19.6	22.9	34.0	23.5	0	3.1	64.6
C16	HZSM-5(1000)	7.9	54.6	8.4	17.7	13.3	6.0	41.5	3.1
C17	SiO_2	7.4	63.9	5.8	13.4	9.7	7.3	32.7	2.8
C18	NaY(4.8)	12.3	18.5	20.4	33.4	21.0	6.7	6.0	4.2

[a] 250°C, 20 atm, SV = 3000 ml (g cat.)$^{-1}$ h^{-1}, H_2/CO_2 = 3. Results after 5 h.
[b] Reference catalysts of the Catalysis Society of Japan; equal amounts of metal catalyst and zeolite (or silica and silica–alumina) physically mixed.
[c] Ratio, SiO_2/Al_2O_3, in parentheses.
[d] Silica–alumina.
[e] MeOH + EtOH + PrOH.
[f] Olefin/(olefin + paraffin) % of C_2, C_3 and C_4.
[g] Branched/(branched + linear) % of C_4, C_5, and C_6.

of iron oxide. With HMOR (C13), US-Y (C14) and HZSM-5(25) (C15), the product contains more of the branched hydrocarbons, and the higher (C_{5+}) hydrocarbons, while the amount of olefin decreases. Therefore, polymerization of the olefins appears to occur to give higher hydrocarbons.

On the other hand, only a slight change in the activity was observed using the catalysts containing zeolites with a lower ratio of SiO_2/Al_2O_3, HY (C12), and higher ratio, HZSM-5(1000) (C16). Similar results were obtained for SiO_2–Al_2O_3 (C11) and SiO_2 (C17). NaY, a Na-type zeolite, increases the conversion, while maintaining the ratio of branched products (C18).

These facts can be explained by using the model involving Na migration via the solid–solid reaction proposed in the preliminary communication [27], which influences the reduction behavior of the iron catalysts and the acidity of the zeolites. Solid–solid reactions have been reported so far for systems of salts of alkaline, alkaline-earth, rare earth and transition metals and noble metals with zeolites [32–41]. It was revealed that all of the alkaline cations (Li, Na,

K, Rb, Cs) can be introduced into the Y-type zeolite via solid–solid reaction between NH_4-Y and respective chlorides [33]. It was also shown that bifunctional catalysts possessing both an acidic and a hydrogenation/dehydrogenation function can be obtained via solid-state ion exchange. In these studies Pd^{2+}, for example, was co-introduced with Ca^{2+} into HZSM-5 via solid–solid reaction of $CaCl_2$/$PdCl_2$ with HZSM-5 and, after reduction of the resulting Pd/Ca/HZSM-5 mixture, finely dispersed Pd^0 particles are formed in the interior of the zeolite structure. The resulting catalyst is active in the hydrogenation of ethylbenzene to ethylcyclohexane or dehydrogenation of ethylcyclohexane to ethylbenzene [34,35].

In the present work, water, formed during the reduction of the catalysts and the hydrogenation of CO_2, seemed to facilitate Na migration, probably with the counter-anion OH$^-$, from the surface of the oxides to the zeolites [32]. Since a large amount of Na on the surface of the iron catalysts inhibits the reduction of the iron oxide, Na migration results in further reduction of the iron oxide [30,31], giving rise to an increase in F–T activity. Branched and higher hydrocar-

bons are then formed via the acidic carbon-homologation on the partially Na^+ ion-exchanged H-type zeolites. The slight change in the activity observed in the reaction with SiO_2–Al_2O_3 (**C11**) and HY (**C12**) arises from the deactivation of the F–T sites by the large number of acidic sites on the zeolite and silica–alumina which competes with the enhancement of reduction arising from Na migration. The absence of apparent changes in activity observed with HZSM-5(1000) (**C16**) and SiO_2 (**C17**), for which the acidic deactivation can be neglected due to the lack of acidic sites, indicates that Na hardly migrates into these materials. However, the remarkable increase of CO_2 conversion observed with the Na-type zeolites (**C18**) suggests that the Na-type zeolites with low SiO_2/Al_2O_3 ratios, having large amounts of $[AlO_4]^-$ and hence relatively high hydrophilicity, occlude H_2O and Na_2O or NaOH inside.

Products containing large amounts of both branched and higher hydrocarbons can be obtained over the composite catalysts of the Fe–Cu–Na (99:1:1.45)/HZSM-5(25) composite catalyst. The modification of the composite catalysts by Na migration via solid–solid reaction seems to be also a facile method for preparing bifunctional catalysts containing F–T catalysts of suitable alkali contents and zeolites with moderate acidity, although a composite catalyst with similar functions can probably be prepared by placing the equilibrium amounts of alkali on each component.

3.3. Reduction behavior of the composite catalysts related to Na migration from the metal oxide catalyst to the zeolite

As described above, Na migration from the surface of the metal-oxide catalyst to the zeolite via solid–solid reaction gave rise to a change of the catalytic activity of the Fe–Cu–Na/zeolite composite catalysts, which was related to the change of the reduction degree of the iron catalysts and the acidity of the zeolites. We investigated the reductive behavior of the same cata-

lysts used in the hydrogenation of carbon dioxide by thermogravimetric analysis. Fig. 1 shows the weight loss vs. reduction time of (a) Fe–Cu–Na (99:1:0.06) (**C1**); (b) Fe–Cu–Na (99:1:1.45) (**C3**); (c) the composite catalyst composed of Fe–Cu–Na (99:1:1.45) and HY(4.8) zeolite (**C12**) in a constant flow of 5% H_2/Ar (100 ml/min, 1 atm) at 250°C. The value of the weight loss at the starting point (0 min) corresponds to the amount of desorbed water before introducing the reductive gas. After introducing 5% H_2/Ar (100 ml/min, 1 atm) of constant flow, two different steps are observed for all the catalysts. The initial step of weight loss of about 0.33 mg is observed in ca. 30 min, which is equivalent to ca. 1/30 of the weight of the catalyst used for analysis. Since there is a low copper content, it is concluded that the first step can be attributed to the reduction of hematite, α-Fe_2O_3, to magnetite, Fe_3O_4. The next step corresponds to the reduction of $Fe_3O_4 \rightarrow \alpha$-Fe and proceeds much more slowly than the first step, which is consistent with previous reports [10–12]. The reduction rate of

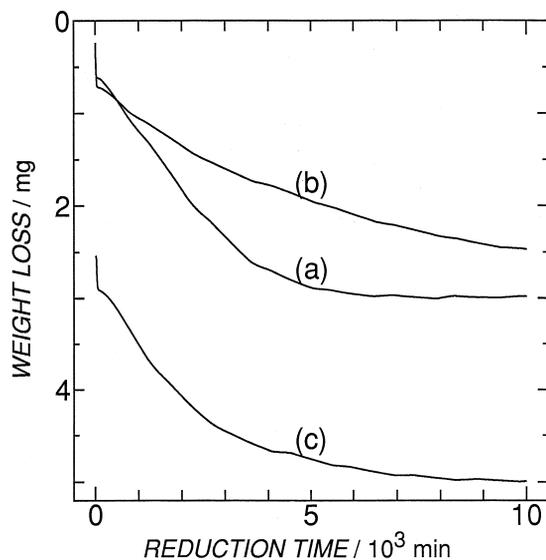Fig. 1. Weight loss vs. reduction time of the catalyst (a) 10 mg of Fe–Cu–Na (99:1:0.06) (**C1**); (b) 10 mg of Fe–Cu–Na (99:1:1.45) (**C3**); (c) the composite catalyst composed of 10 mg of Fe–Cu–Na (99:1:1.45) and 10 mg of HY (4.8) zeolite (**C12**), in a constant flow of 5% H_2/Ar (100 ml/min, 1 atm) at 250°C.

the first step for the Na-rich catalyst **C3** is almost the same as for the Na-poor catalyst **C1**. However, the second step reduction proceeds much more slowly for the Na-rich catalyst **C3** than for the Na-poor catalyst **C1**; this is consistent with the previous observation that alkali addition inhibits the reduction of iron oxide because of the weakening of the metal–hydrogen bond by electronic effects [30,31]. By physically mixing the Na-rich catalyst **C3** with the HY (4.8) zeolite, the reduction rate of the second step is drastically increased and is of the same order as that of the Na-poor catalyst **C1**. This means that the inhibition of reduction as a result of the presence of Na has disappeared, consistent with the migration of Na from the oxides surface to the zeolite.

Table 4 summarizes the influence of physical mixing with the zeolites on the second reduction step, $Fe_3O_4 \rightarrow \alpha$-Fe, of the Fe–Cu–Na catalysts. $T_{1/2}$ denotes the reduction time in which half of the catalyst sample was reduced from magnetite Fe_3O_4 to α-Fe. It is obvious that there was almost no effect on the reduction rate as a result of physically mixing the HY zeolite with the Na-poor catalyst **C1**. On the other hand, physical mixing increases the rate of reduction of the Na-rich catalyst **C3**, as a result of the increased efficiency of Na migration. The effect is more significant for H-type zeolites having lower SiO_2/Al_2O_3 ratio. The effect was also observed for NaY(4.8), in which occlusion of sodium in the form of NaOH was probably facilitated by absorbed water. These observations confirmed the explanation of the results of the hydrogenation of carbon dioxide over the same composite catalysts as described above.

X-ray diffraction measurements also qualitatively supported the account of Na migration. There were no distinct differences of the XRD patterns of HY zeolite in the composite catalyst **C12** before and after reaction. However, for the composite catalyst Fe–Cu–Na (99:1:27)/HY the reflections from the framework of the HY zeolite weakened and broadened, indicating the crystallinity of the zeolite decreased during the reaction. This composite catalyst contains about twenty times more Na than **C3**, which allows a large amount of Na to migrate from the surface of the metal oxides to the zeolite, resulting in a lower hydrothermal stability and a damage of the zeolite lattice under the reaction conditions [42].

4. Conclusions

Composite catalysts containing iron-based F–T catalysts and zeolites were studied for the hydrogenation of carbon dioxide at 250°C. It seemed that sodium migration from the surface of the F–T catalyst to the zeolite gave rise to change of the reduction degree of the Fe catalyst and the acidity of the zeolite, and therefore to the change of catalytic activity of the composite catalyst. TG and XRD measurements supported the account of Na migration, while more direct evidence remains desired. The present work demonstrated that branched and higher hydrocarbons can be obtained in good yields by using a mixture containing an iron-based catalyst with moderate alkali content and a zeolite with suitable acidity.

Table 4
The variation in reduction rates of Fe–Cu–Na catalysts on physically mixing with zeolites

Cat.	Catalyst	$T_{1/2}$ (10^3 min[a])
C1	Fe–Cu–Na (99:1:0.06)	2.1
C5	Fe–Cu–Na (99:1:0.06)/HY(4.8)	2.2
C3	Fe–Cu–Na (99:1:1.45)	5.6
C12	Fe–Cu–Na (99:1:1.45)/HY(4.8)	2.2
C15	Fe–Cu–Na (99:1:1.45)/HZSM-5(25)	2.7
C16	Fe–Cu–Na (99:1:1.45)/HZSM-5(1000)	3.5
C18	Fe–Cu–Na (99:1:1.45)/NaY(4.8)	2.4

[a]Reduction time in which half of the catalyst sample was reduced from magnetite, Fe_3O_4, to α-Fe.

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