Tailoring effective FeO_x/SiO_2 catalysts in methane to formaldehyde partial oxidation

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Received 22 October 2001; accepted 24 January 2002

A preparation method of highly effective methane to formaldehyde partial oxidation (MPO) FeO_x/SiO_2 catalysts (Fe 0.09–0.43 wt%) is reported, based on "adsorption–precipitation" (ADS/PRC) of Fe^{II} ions under controlled conditions. The performance of ADS/PRC catalysts in the MPO reaction at 650 °C has been compared with that of conventional systems prepared by "incipient wetness" (INC/WET) of silica carriers with aqueous solutions of Fe^{III}. The ADS/PRC method, likely enabling a higher dispersion of the active phase, provides very effective MPO catalysts featuring CH_4 turnover frequency (TOF) and HCHO productivity (STY_{HCHO}) values larger than those of the counterpart INC/WET systems.

KEY WORDS: methane partial oxidation; formaldehyde; FeO_x/SiO_2 catalysts; preparation method; Fe precursor; dispersion; HCHO productivity; turnover frequency.

1. Introduction

A large number of research papers devoted during the past decade to the catalytic partial oxidation of methane to formaldehyde (MPO) allowed the peculiar functionality of the silica surface towards HCHO formation to be highlighted [1–8]. The preparation method affects the catalytic performance of commercial silica samples, according to the activity scale precipitation > sol-gel > pyrolysis [1,2,5,6], since it determines the density of "strained siloxane bridges", early claimed to be the active sites in MPO [1,6]. Actually, by adopting a "continuous flow recirculation" reactor, a "precipitated" silica sample (Si 4-5P grade, Akzo product) ensured quite high CH_4 conversion (35–60%) and HCHO selectivity (30–56%) values in the range 650–700 °C [7]. Such promising catalytic performance, really among the best thus far vindicated, prompted us to investigate in some detail the kinetics and mechanism of the MPO reaction on such precipitated silica catalyst [9,10] as well as to ascertain the origin of its catalytic functionality [6,11]. On this account, we found that the intrinsic activity of various commercial silicas in MPO, besides the concentration of strained siloxane bridges [6], can also be related to the extent of Fe^{3+} ions incorporated into the matrix during preparation [11]. Then, direct relationships between the concentration of "isolated" Fe^{3+} species in a rhombic-like coordination and reaction rate or HCHO productivity (STY_{HCHO}) were outlined, whereas, Fe_2O_3 clusters, bearing Fe^{3+} ions in an octahedral symmetry, mostly drive CO_x formation owing to a high availability and mobility of lattice oxygen ions [11]. Such findings undoubtedly pointed to dispersion as the key factor affecting the performance of the FeO_x/SiO_2 system in MPO [11], stimulating further research efforts aimed at disclosing effective preparation methods enabling a high dispersion of the active phase and then an improved functionality of FeO_x/SiO_2 catalysts in MPO [11,12]; namely, a preparation method based on the adsorption–precipitation of Fe^{II} ions on silica matrices [13–15] under controlled pH and anaerobic conditions has been exploited [12]. Notably, the enhancement of dispersion in ZSM-5 supported FeO_x systems is actually pursued to attain very effective SCR catalysts for NO_x emissions abatement [13,14]. In fact, Feng and Hall [13,14] found that adsorption of Fe^{2+} ions from "O_2-free" aqueous solutions of FeC_2O_4 lead to very effective, stable and durable $DeNO_x$ catalysts. Nonetheless, catalytic performance, hydrothermal stability, Fe-exchange capacity and resistance to poisoning were found to strongly depend upon the ZSM-5 carrier [15], as subtle differences in the surface chemistry of parent zeolites, induced by the synthesis procedures, involved remarkable differences in the catalytic behaviour of FeZSM-5 systems [15].

Therefore, this contribution is aimed at providing basic evidence of the suitability of the preparation method based on adsorption–precipitation of Fe^{II} precursors from aqueous solutions under anaerobic and controlled pH conditions to attain highly dispersed FeO_x/SiO_2 systems featuring a remarkable catalytic performance in MPO.

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1011-372X/02/0500-0069/0

2. Methods

2.1. Background to Fe^{II} adsorption–precipitation preparation method

The marked tendency of Fe^{3+} ions to form the insoluble hydroxide ($Fe(OH)_3$, 1.2×10^{-38} K_{ps}) in aqueous solution prompted since 1969 the use of Fe^{2+} precursors to attain a high dispersion of the active phase, basically, across the ZSM-5 zeolite support [14]. That is, conventional impregnation methods based on the "incipient wetness", "ion exchange" or "electrostatic adsorption" of Fe^{III} precursors, preventing a timely interaction of positive hydroxo-ions with the negatively polarized hydroxyls of acidic oxide carriers at $pH > 6$, cannot in principle enable a high dispersion of Fe^{III} species in supported systems [13,14]. Moreover, special preparation methods like gas-phase grafting of Fe^{3+} precursors (*i.e.* $FeCl_3$), though enabling a high dispersion of the iron phase, imply the deposition of foreign ions (*i.e.* Cl^-) on supports, namely requiring further treatment steps for their removal [14].

Then, the adsorption–precipitation of Fe^{2+} ions (ADS/PRC) in aqueous solutions, under O_2-free (N_2) atmosphere and controlled pH conditions [13–15] was exploited to achieve a higher dispersion of MPO FeO_x/SiO_2 catalysts [11,12]. Such a preparation route, preventing the formation of insoluble hydroxides ($Fe(OH)_2$, 1.8×10^{-12} K_{ps}) at acidic (<7) pH values, involves an effective interaction of the negatively polarised silica surface with Fe^{2+} ions (pH 7–8) allowing thus for a selective tailoring of "isolated" Fe^{3+} species onto the matrix [12–14].

2.2. Catalysts

A series of silica supported iron catalysts (*x*-FS) was prepared by the ADS/PRC method according to the following experimental procedure. Namely, 10 g of a powdered silica carrier were put into 0.3 l of distilled water with a resulting pH of ~4.5. The suspension was vigorously stirred (~1000 rpm) and kept under a nitrogen flow (~100 stp cm^3/min) for 1 h at room temperature to remove any dissolved oxygen, thus avoiding any further air admission. Then, an amount of $FeSO_4 \cdot 7H_2O$ corresponding to the designed Fe loading was added to the stirred suspension at room temperature, raising progressively (30 min) the pH to a value of 7.0–7.5 by addition of a 10% NH_4OH solution. The suspension was kept at the final pH value under stirring and N_2 bubbling for 1 h to attain a complete adsorption of precursor, the efficiency of the ADS/PRC preparation method, in terms of amount of Fe^{2+} adsorbed, resulting in better than 98%. Thereafter, the catalyst was filtered, repeatedly washed with distilled water, dried at 100 °C and then calcined at 600 °C in air for 16 h.

For the sake of comparison, a series of silica supported iron catalysts (*x*-FS) was prepared by the incipient wetness method, using powdered silica samples and aqueous solutions (pH ~3) of $Fe(NO_3)_3$. After impregnation, the catalysts were dried overnight at 100 °C and then calcined at 600 °C for 16 h.

All the FeO_x/SiO_2 catalysts were prepared using two precipitated silica samples, namely Si 4-5P (Si 4-5P grade; Akzo product) and F5 (F5; Akzo product), preliminarily calcined at 600 °C for 16 h in air, as carriers. The list of catalysts, along with the relative code, preparation method, Fe content (wt%), as determined by AAS measurements, BET surface area (SA_{BET}, $m^2\,g^{-1}$) and surface Fe loading (SL, $Fe_{at}\,nm^{-2}$) values, is reported in table 1.

2.3. Catalyst testing

Catalyst testing in the MPO was performed by a specifically designed recirculation batch reactor operating at 650 °C and 1.7 atm total pressure [2,5,8–10] with a flow rate of 1000 stp $cm^3\,min^{-1}$ ($He:N_2:CH_4:O_2 = 6:1:2:1$) and a catalyst sample of 0.050 g (τ, 125.6 $atm\,s\,g\,mol^{-1}$), unless otherwise specified.

Table 1
List of SiO_2 and FeO_x/SiO_2 samples

Code	SiO_2 support	Preparation method	Fe precursor	Fe loading (wt%)	SA_{BET} ($m^2\,g^{-1}$)	SL ($Fe_{at}\,nm^{-2}$)
Si 4-5P	Si 4-5P	–	–	0.02	385	0.011
F5	F5	–	–	0.015	607	0.003
1-FS	F5	INC/WET	Fe^{III}	0.095	593	0.018
2-FS	Si 4-5P	INC/WET	Fe^{III}	0.10	402	0.027
3-FS	Si 4-5P	INC/WET	Fe^{III}	0.43	398	0.118
FS-1	Si 4-5P	ADS/PRC	Fe^{II}	0.35	399	0.096
FS-2	F5	ADS/PRC	Fe^{II}	0.09	601	0.081
FS-3	F5	ADS/PRC	Fe^{II}	0.37	597	0.018

3. Results and discussion

The first evidence of a different effectiveness of ADS/PRC and INC/WET preparation routes in promoting dispersion of Fe^{III} on the silica carriers stems from a different colour of the two series of catalysts, mostly at Fe loadings higher than 0.1 wt%. Namely, while a typical brownish dye of INC/WET catalysts, the intensity rising with loading, likely signals the presence of Fe_2O_3 clusters at any loading (0.09–0.43 wt% Fe), ADS/PRC samples were colourless up to the highest investigated Fe loading (0.43 wt%).

The effectiveness of the ADS/PRC method in promoting the dispersion of the supported phase, and consequently the activity of FeO_x/SiO_2 systems in MPO [11], has been evaluated by comparing the performance of catalysts prepared using either Si 4-5P or F5 silicas carriers by INC/WET and ADS/PRC respectively. Then, the activity data (T_R, 650 °C) of the differently Fe-loaded catalysts in the MPO reaction, with reference to Si 4-5P and F5 silica supports, are presented in table 2 in terms of hourly CH_4 conversion ($X_{CH_4,h}$, %), product selectivity (S_X, %) and reaction rate (rate, $\mu mol_{CH_4}\,s^{-1}\,g^{-1}$), while the relative space–time yield (STY_{HCHO}, $g\,kg_{cat}^{-1}\,h^{-1}$) and CH_4 turnover frequency (TOF, s^{-1}) values, calculated on the basis of the actual Fe loading (see table 1), are compared in figure 1.

According to our previous findings [11], Fe-addition always results in a marked promoting effect on the activity of whatever silica support, though it is evident that the ADS/PRC route is considerably more effective than conventional INC/WET in enhancing the catalytic performance of the FeO_x/SiO_2 system in MPO at any loading [12].

In particular, the bare Si 4-5P silica support features an hourly CH_4 conversion of 3.5%, corresponding to a methane TOF of 3.0 s^{-1}, along with a S_{HCHO} value of 80% (S_{CO}, 14%; S_{CO_2}, 6%) which account for a STY_{HCHO} of 310 $g\,kg_{cat}^{-1}\,h^{-1}$ (figure 1). In spite of its larger surface area (table 1), the F5 silica carrier displays both lower activity ($X_{CH_4,h}$, 2.9%) and S_{HCHO} (64%) with respect to the Si 4-5P sample, resulting in a STY_{HCHO} of 195 $g\,kg_{cat}^{-1}\,h^{-1}$. Yet while a TOF value of 3.0 s^{-1} (figure 1), equal to that of the Si 4-5P silica catalyst, proves that the decrease in activity is the consequence of the lower Fe content (see table 1), the drop in S_{HCHO}, counterbalanced by a spectacular rise in S_{CO}, reflects the higher tendency of such a system to drive the consecutive oxidation of the primary oxidation product [1–5,7–11], likely because of the larger development in surface area preventing its fast removal from the catalytic zone.

Table 2
Activity data of SiO_2 and FeO_x/SiO_2 catalysts in MPO at 650 °C

Sample	W_{cat} (mg)	$X_{CH_4,h}$ (%)	S_{HCHO} (%)	S_{CO} (%)	S_{CO_2} (%)	rate ($\mu mol_{CH_4}\,s^{-1}\,g^{-1}$)
Si 4-5P	50	3.5	80	14	6	3.6
F5	50	2.7	65	27	8	2.8
1-FS	50	8.6	55	28	17	8.8
2-FS	50	13.4	56	22	22	13.8
3-FS	50	13.2	39	30	31	13.6
FS-1	50	37.2	33	29	31	38.3
FS-2	50	14.9	64	22	12	15.0
FS-3	50	34.2	35	28	27	35.4
FS-1	5.0	4.6	55	23	22	47.3

Addition of 0.10 wt% of Fe to the Si 4-5P silica sample by INC/WET (2-FS) implies an ~4-fold rise in $X_{CH_4,h}$ (13.4%) and reaction rate (13.8 $\mu mol_{CH_4}\,s^{-1}\,g^{-1}$) along with a lowering in S_{HCHO} from 80 to 56% (table 2). Notably, with reference to the Si 4-5P silica carrier, the above figures account for a decrease in TOF from 3.0 to 2.1 s^{-1} and a marked rise in STY_{HCHO} from 310 to 830 $g\,kg_{cat}^{-1}\,h^{-1}$, respectively (figure 1). A comparable amount of Fe (0.095 wt%) added to F5 silica carrier still by INC/WET (1-FS) attains an even lower promoting effect on the activity ($X_{CH_4,h}$, 8.6%), while the product distribution (S_{HCHO}, 55%) looks similar to

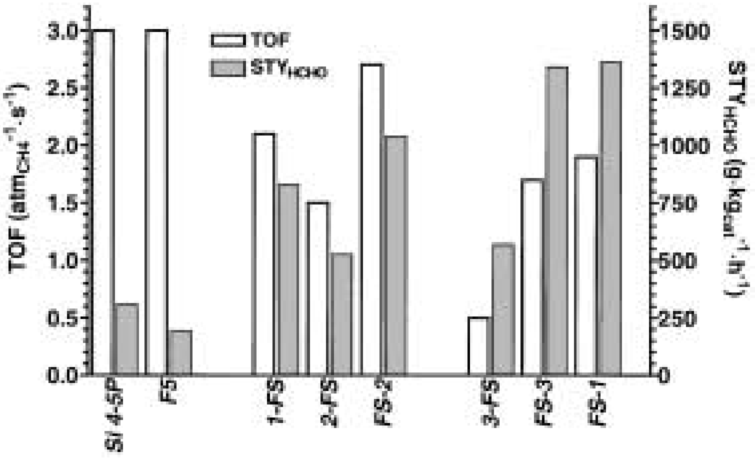

Figure 1. MPO on SiO_2 and FeO_x/SiO_2 catalysts. Methane turnover frequency (TOF, s^{-1}) and space–time yield (STY_{HCHO}, $g\,kg_{cat}^{-1}\,h^{-1}$) values at 650 °C.

that of the previous sample. These catalytic data are reflected in the lower reaction rate ($8.6\,\mu mol_{CH_4}\,s^{-1}\,g^{-1}$) and STY_{HCHO} ($525\,g\,kg_{cat}^{-1}\,h^{-1}$) values which, on the basis of a TOF equal to $1.5\,s^{-1}$ (figure 1), is ascribable to a poorer dispersion of the active phase [11]. On the other hand, the F5 silica-supported FS-2 system, bearing 0.09 wt% of Fe loaded by the ADS/PRC method, displays a much higher activity ($X_{CH_4,h}$, 14.9%,) along with an improved S_{HCHO} (64%) accounting for TOF and STY_{HCHO} values equal to $2.7\,s^{-1}$ and $1040\,g\,kg_{cat}^{-1}\,h^{-1}$ respectively, considerably larger than those of both 1-FS and 2-FS catalysts (see figure 1).

Addition of 0.43 wt% of Fe^{III} to Si 4-5P carrier by INC/WET (3-FS) even has a negative effect on the most important parameters (S_{HCHO}, TOF, STY_{HCHO}) featuring the performance of MPO catalysts, with respect to the 2-FS system [11]. Indeed, while an $X_{CH_4,h}$ of 13.2%, practically equal to that of the 2-FS sample, and a lower S_{HCHO} (39%) accounts for a STY_{HCHO} of only $570\,g\,kg_{cat}^{-1}\,h^{-1}$, the rise of both S_{CO} (30%) and S_{CO_2} (31%) and the marked decrease in TOF ($0.5\,s^{-1}$) altogether are diagnostic of a weak catalytic functionality consequent to a drop in FeO_x dispersion [11]. Indeed, despite the comparable Fe loading (0.35 wt%), the FS-1 sample, obtained by ADS/PRC of Fe^{2+} ions on the Si 4-5P silica, features an impressive activity ($X_{CH_4,h}$, 37.2%) larger by about one order of magnitude than that of the relative silica carrier and about three times higher than that of the counterpart 3-FS catalyst, though S_{HCHO} (33%) stays at a comparable level with the former system. Considerably higher TOF and STY_{HCHO} values, equal to $1.9\,s^{-1}$ and $1360\,g\,kg_{cat}^{-1}\,h^{-1}$ respectively, indicate that the FS-1 catalyst is about four times more active than the counterpart 3-FS sample, though preserving a satisfactory functionality towards HCHO formation.

Such findings undoubtedly prove that the ADS/PRC method confers to FeO_x/SiO_2 catalysts a considerably superior activity in MPO with respect to the conventional INC/WET route, also irrespective of the silica carrier. In fact, considering the FS-3 sample (0.37 wt% Fe), prepared by ADS/PRC on F5 silica carrier, an activity–selectivity pattern quite similar to that of the homologous FS-1 system ($X_{CH_4,h}$, 34.2%) is noticed, while also the TOF and STY_{HCHO} values, equal to $1.7\,s^{-1}$ and $1340\,g\,kg_{cat}^{-1}\,h^{-1}$ respectively, compare well with the values of the latter sample (figure 1).

Due to the high value of CH_4 conversion (~13.5%) of the above two systems which could result in the reaction kinetics being controlled by the O_2 conversion level [9,10], by tuning a timely decrease in contact time (W_{cat}, 0.005 g; τ, $12.6\,atm\,s\,g\,mol^{-1}$), the activity–selectivity pattern of the FS-1 catalyst at a CH_4 conversion level comparable with that of the Si 4-5P silica carrier has been investigated. Such data, also included in table 2, outline an $X_{CH_4,h}$ of 4.6% corresponding to a TOF equal to $2.3\,s^{-1}$, larger by ~20% than the value ($1.9\,s^{-1}$) at higher τ. An S_{HCHO} level of 55% coupled to such a high specific activity implies a steep rise in STY_{HCHO} to a value of $2810\,g\,kg_{cat}^{-1}\,h^{-1}$. Notably, such a figure results in one order of magnitude greater than that of the related bare silica sample and, really, represents a breakthrough in view of the potential industrial exploitation of the MPO reaction [12].

In conclusion, the above results prove the superior efficiency of the ADS/PRC preparation method in promoting the catalytic functionality of the FeO_x/SiO_2 system at any loading and its potential in tailoring FeO_x/SiO_2 catalysts very effectively in MPO reaction.

Acknowledgments

This work has been realized in the framework of a research contract (August 2000–July 2002) between SÜD Chemie AG (München, Germany) and the University of Messina (Messina, Italy).

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