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Iron-containing heterogeneous catalysts for partial oxidation of methane and epoxidation of propylene

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Abstract

Mesoporous molecular sieves containing iron sites with different dispersions and environments were studied for the partial oxidation of methane and the epoxidation of propylene. The tetrahedral Fe(III) sites incorporated inside the framework of SBA-15 showed higher HCHO selectivity under a similar CH_4 conversion than the oligomeric FeO_x clusters located in the mesopores in the partial oxidation of CH_4 by O_2. HCHO selectivity of the FeO_x clusters in SBA-15 could be improved by the modification with either an acidic group (e.g., phosphate) or an alkali metal ion, which increased the dispersion or changed the local coordination environment of iron species. The catalyst containing $FePO_4$ clusters formed by the modification with phosphate exhibited the best catalytic performances for HCHO formation. This catalyst also showed uniquely high selectivities to HCHO and CH_3OH as N_2O was used as the oxidant for the partial oxidation of CH_4. For the epoxidation of propylene to propylene oxide (PO), the modification of the FeO_x/SBA-15 with an alkali metal salt typified by KCl was effective. Among many SBA-15-supported transition metal oxides modified by KCl, the KCl-FeO_x/SBA-15 showed the best catalytic performances for the epoxidation of propylene by N_2O. The comparative studies using N_2O and O_2 as the oxidant revealed that N_2O was necessary for PO formation over the KCl-FeO_x/SBA-15 catalyst.

Keywords: Iron; Mesoporous silica; Methane; Selective oxidation; Propylene; Epoxidation

1. Introduction

The exploitation of iron as the active site in synthetic catalysts for selective oxidation of hydrocarbons has received extensive research attention because iron is the active center in monooxygenase enzymes such as cytochrome P-450 and methane monooxygenase. There are numerous studies on homogeneous catalytic systems using iron compounds or iron complexes for the selective oxidation of hydrocarbons [1,2]. However, iron-based heterogeneous oxidation catalytic systems reported so far are limited. Fe-ZSM-5 catalyst combined with N_2O oxidant was effective for the selective oxidation of benzene to phenol [3]. Although it was shown that the adsorbed oxygen (α-oxygen) pre-generated by the decomposition of N_2O over the Fe-ZSM-5 may react with CH_4 even at room temperature to form surface methoxy species, the steady-state catalytic oxidation of CH_4 with N_2O at a temperature needed for N_2O decomposition only produced CO and CO_2 as the main products with a minor amount of CH_3OH [3,4]. Wang and Otsuka [5–8] showed in a series of studies that $FePO_4$ was an efficient catalyst for the partial oxidation of CH_4 to HCHO by O_2 and to oxygenates including CH_3OH and HCHO by O_2–H_2 gas mixture or N_2O. Kobayashi et al. [9–11] clarified that a small amount of Fe^{3+} doped in silica could catalyze the partial oxidation of CH_4 to HCHO by O_2, and it was proposed that the small amount of mononuclear Fe^{III} probably incorporated into the silica matrix was responsible for HCHO formation. Arena and Parmaliana [12–14] adopted an ‘‘adsorption–precipitation’’ method for the synthesis of the FeO_x/SiO_2 samples containing relatively higher concentration of iron species with high dispersion and investigated their catalytic activities for partial oxidation of CH_4 by O_2.

A few studies have contributed to the epoxidation of alkenes using Fe-containing heterogeneous catalysts. Fe-MCM-41 with Fe^{III} in the framework of MCM-41 could catalyze the epoxidation of styrene with diluted H_2O_2 [15]. Single-site Fe^{III} centers grafted on the inner surfaces of SBA-15 showed a high efficiency for the epoxidation of various alkenes with

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H_2O_2 [16]. Duma and Hönicke once reported an interesting gas-phase epoxidation of propylene by N_2O over a Na^+-added Fe_2O_3/SiO_2 catalyst [17].

Most of the existing researches seem to suggest that a high dispersion of iron species is necessary for the selective oxidation reactions since iron oxides such as α-Fe_2O_3 tend to catalyze the over-oxidation of hydrocarbons to CO and CO_2. More detailed elucidations of structure–reactivity relationships are important for the development of efficient iron-based heterogeneous selective oxidation catalysts. Mesoporous materials possess ordered porous structures, and the active components tailored in their nano-ordered spaces may have improved catalytic performances. We have clarified that MCM-41 and SBA-15 are superior catalyst supports for $FePO_4$, VO_x and MoO_x for the partial oxidation of CH_4 [18–21]. Moreover, iron may have different locations and different local structures in a mesoporous silica, e.g., FeO_x clusters in mesopores or isolated Fe^{III} in framework positions. In a previous paper, we showed that the Fe^{III} in the framework of MCM-41 was more efficient than the FeO_x clusters for the conversion of CH_4 to HCHO by O_2 [22]. The environment of the iron sites can further be modified by the presence of acidic groups or alkali metal ions. We have been working on the elucidation of the relationships between the structures and environments of the active iron sites introduced into mesoporous silica and their catalytic behaviors in selective oxidation reactions. In the present paper, we present some of our recent research results on the partial oxidation of CH_4 to useful oxygenates and the epoxidation of propylene, which are two highly desirable but very difficult reactions.

2. Experimental

Iron-containing SBA-15 materials were prepared by the following methods. In the direct synthesis, an iron source ($FeCl_3$) was added into the synthesis gel containing the silica source ($SiCl_4$) and the template (Pluronic P123 triblock copolymer). After hydrothermal synthesis, the resultant solid was filtered, washed, dried and finally calcined at 550 or 650 °C for 6 h. The obtained samples were denoted as Fe-SBA-15. The conventional impregnation method was also applied to the preparation of iron-containing SBA-15 samples (denoted as FeO_x/SBA-15) using an ethanolic solution of $[Fe(acac)_3]$ (acac, acetylacetonate). The FeO_x/SBA-15 was modified by various acid and alkaline additives including P, S, B, Li, Na, K, Rb and Cs by impregnation of the FeO_x/SBA-15 with an aqueous solution of phosphate, sulphate, borate or an alkali metal salt.

The catalysts were characterized by XRD, diffuse reflectance UV–vis, and Raman spectroscopic measurements. XRD was performed with a Panalytical X'Pert Pro Super X-ray diffractometer with Cu Kα radiation. Diffuse reflectance UV–vis spectra were recorded on a Varian Cary-5000 spectrometer equipped with a diffuse-reflectance accessory. Raman spectroscopic measurements were carried out with a Renishaw UV–vis Raman System 1000R. The UV-line at 325 nm from a Kimmon IK3201R-F He–Cd laser was used as the exciting source to avoid the influence of fluorescence.

The partial oxidation of CH_4 and the epoxidation of C_3H_6 were carried out using a fixed-bed flow reactor (quartz tube) operated at atmospheric pressure. The products were analysed by on-line gas chromatography. All the lines and valves between the exit of the reactor and the gas chromatographs were heated to 120 °C to prevent the condensation of products. Porapak T column was used for the separation of CH_3OH and HCHO in the case of CH_4 partial oxidation, and for the separation of PO, acrolein, allyl alcohol, acetone, propionaldehyde and acetaldehyde in the case of C_3H_6 oxidation. The separations of other products and the remaining reactants in both cases were achieved by Porapak Q and Molecular Sieve 5A columns.

3. Results and discussion

3.1. Comparative studies of iron-containing mesoporous materials synthesized by different method for partial oxidation of CH_4 by O_2

In a previous paper [22], we carried out comparative studies with Fe-MCM-41 synthesized by two different methods, i.e., the direct hydrothermal (DHT) and the template-ion exchange (TIE) methods, and arrived at a conclusion that the iron sites isolated in the framework in the Fe-MCM-41-DHT were more active and selective than the oligomeric FeO_x in the Fe-MCM-41-TIE for the partial oxidation of CH_4 by O_2. However, the HCHO selectivity obtained over the Fe-MCM-41-DHT catalyst was still very low (ca. 15% at a 2% CH_4 conversion).

We recently found that, as compared with MCM-41, SBA-15 was a better support for the loadings of MoO_x [19], VO_x [20,21] and $FePO_4$ [23] for the partial oxidation of CH_4 by O_2 due to its larger pore diameter and more inert property without any acid sites. Thus, here we first compare the catalytic performances of the Fe-SBA-15 prepared by the direct synthesis and the FeO_x/SBA-15 prepared by the impregnation. It should be noted that only ca. 0.1 wt% Fe could be incorporated into SBA-15 by the

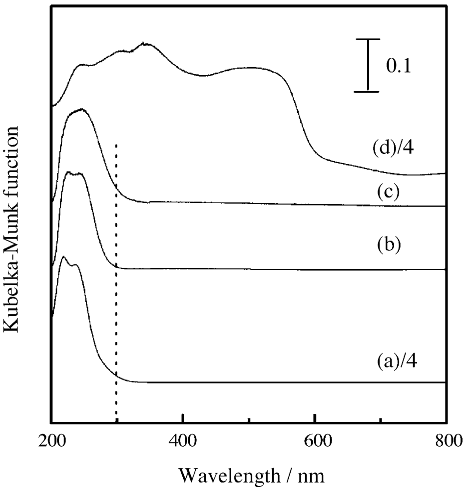

Fig. 1. UV–vis spectra of the iron-containing SBA-15 together with reference samples. (a) Fe-MFI, (b) 0.1 wt% Fe-SBA-15, (c) 0.1 wt% FeO_x/SBA-15 and (d) α-Fe_2O_3.

direct synthesis irrespective of the amount of iron added in the synthesis mixture possibly because SBA-15 was prepared in a strong acid medium [24].

Fig. 1 shows the diffuse reflectance UV–vis spectra of the Fe-SBA-15 and the FeO$_x$/SBA-15 together with two reference samples, the Fe-MFI zeolite (Si/Fe = 64) and α-Fe$_2$O$_3$, in which iron atoms are in isolated tetrahedral and aggregated octahedral states, respectively. Distinctly different from α-Fe$_2$O$_3$, both the Fe-SBA-15 and the FeO$_x$/SBA-15 did not show obvious absorption in visible region, indicating that there were no α-Fe$_2$O$_3$ or heavily aggregated iron oxide particles in these samples. The main difference of the two iron-containing SBA-15 samples lies in the position of the absorption edge, which reflects the bandgap energy (E_g), and the E_g is related to the domain size (dispersion) and the coordination structure of the transition metal oxides or ions [25]. We have calculated the E_g values (Table 1) for the Fe–O band from the UV–vis spectra using the method suggested by Weber [25]. The result that the E_g value for the Fe-SBA-15 is very close to that for the Fe-MFI while the E_g for the FeO$_x$/SBA-15 is lower indicates that the iron sites in the Fe-SBA-15 are mostly isolated in the framework of SBA-15, whereas the FeO$_x$/SBA-15 probably contains oligomeric FeO$_x$ clusters.

Fig. 2 shows the changes in HCHO selectivity as a function of CH$_4$ conversion obtained at 450–650 °C over the Fe-SBA-15 and the FeO$_x$/SBA-15. In the whole range, the Fe-SBA-15 possessed higher HCHO selectivity than the FeO$_x$/SBA-15 at a certain CH$_4$ conversion. This strongly suggests that the iron sites isolated in the framework of SBA-15 are more selective than the oligomeric FeO$_x$ clusters for the partial oxidation of CH$_4$ to HCHO by O$_2$. This conclusion is consistent with that achieved with the Fe-MCM-41 prepared by the DHT and the TIE methods [22], but the HCHO selectivity over the Fe-SBA-15 is remarkably higher than that over the Fe-MCM-41. By optimizing the reaction conditions, we obtained a 2.1% yield (single-pass) to HCHO with a selectivity of 52%, and at the same time, the HCHO space time yield was 22.3 mmol g(cat)$^{-1}$ h^{-1}, affording a turnover frequency for HCHO formation of 1245 mol (mol-Fe)$^{-1}$ h^{-1}.

Table 1
Bandgap energy (E_g) values for the Fe–O band of iron-containing samples

Sample	E_g (eV)
α-Fe$_2$O$_3$	2.10
Fe-MFI	4.68
0.1 wt% FeO$_x$/SBA-15	4.30
0.1 wt% Fe-SBA-15	4.62
1 wt% FeO$_x$/SBA-15	4.05
P-1 wt% FeO$_x$/SBA-15 (P/Fe = 0.5)	4.08
P-1 wt% FeO$_x$/SBA-15 (P/Fe = 1)	4.10
B-1 wt% FeO$_x$/SBA-15 (B/Fe = 0.5)	4.40
S-1 wt% FeO$_x$/SBA-15 (S/Fe = 0.5)	4.42
Li-1 wt% FeO$_x$/SBA-15 (Li/Fe = 0.5)	4.48
Na-1 wt% FeO$_x$/SBA-15 (Na/Fe = 0.5)	4.62
K-1 wt% FeO$_x$/SBA-15 (K/Fe = 0.5)	4.58
Rb-1 wt% FeO$_x$/SBA-15 (Rb/Fe = 0.5)	4.57
Cs-1 wt% FeO$_x$/SBA-15 (Cs/Fe = 0.5)	4.61

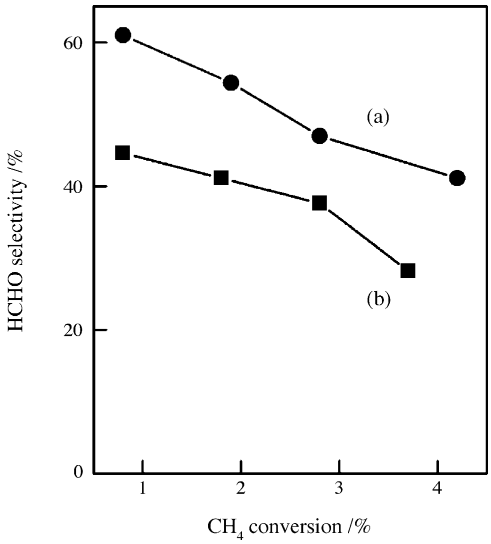

Fig. 2. Catalytic performances of the 0.1 wt% Fe-SBA-15 (a) and the 0.1 wt% FeO$_x$/SBA-15 (b) for partial oxidation of CH$_4$ by O$_2$. Reaction conditions: T = 450–650 °C; W = 0.1 g; F = 120 mL min^{-1}; P(CH$_4$) = P(O$_2$) = 33.8 kPa.

3.2. Modifications of FeO$_x$/SBA-15 with acid and alkaline additives for partial oxidation of CH$_4$ by O$_2$

To uncover the influences of the acid or alkaline environment of iron sites on their catalytic properties in the partial oxidation of CH$_4$, we investigated the effects of the modifications of the FeO$_x$/SBA-15 with various acid and alkaline additives. We had chosen the FeO$_x$/SBA-15 with an iron content of 1 wt% for these investigations.

As shown in Fig. 3, in the plot of HCHO selectivity versus CH$_4$ conversion, the curves for all of the modified FeO$_x$/SBA-15 were above that for the FeO$_x$/SBA-15 without an additive. Thus, all the acid and alkaline additives investigated could enhance the selectivity to HCHO. Among these additives, the phosphate (expressed as P) was the best for HCHO formation. For the alkali metal ion additives, HCHO selectivity decreased with the sequence of Li$^+$ > Na$^+$ > K$^+$ > Rb$^+$ > Cs$^+$, indicating that the alkaline property is detrimental to HCHO formation.

To clarify why these modified catalysts showed higher HCHO selectivity than the FeO$_x$/SBA-15, we carried out diffuse reflectance UV–vis spectroscopic measurements for these samples, and the E_g values of Fe–O band calculated are listed in Table 1. The E_g increased significantly for all of the modified FeO$_x$/SBA-15 samples except for the P-FeO$_x$/SBA-15, suggesting that the dispersion of iron species was raised by most of these additives. Thus, the higher dispersion of iron species in the presence of the additives led to the higher HCHO selectivity.

Fig. 4 shows the Raman spectra of the acid additive-modified FeO$_x$/SBA-15 samples. The FeO$_x$/SBA-15 without the additive gave two main Raman bands at 982 and 1078 cm^{-1} in the region of 900–1200 cm^{-1}, possibly ascribed to the dispersed iron species. These bands were not significantly changed for the S- and B-modified FeO$_x$/SBA-15. However, for the P-FeO$_x$/SBA-15, the two bands shifted together and the peak positions became similar to those for FePO$_4$ at 1015 and

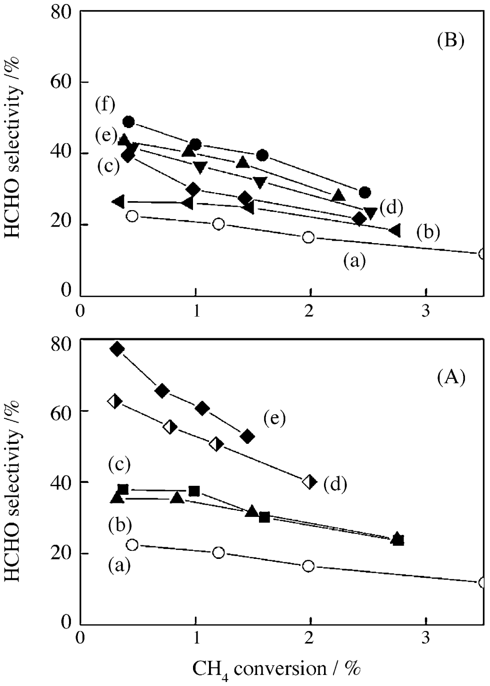

Fig. 3. Catalytic performances of the FeO$_x$/SBA-15 modified by various additives for the partial oxidation of CH$_4$ by O$_2$. (A): (a) 1 wt% FeO$_x$/SBA-15, (b) B-1 wt% FeO$_x$/SBA-15 (B/Fe = 0.5), (c) S-1 wt% FeO$_x$/SBA-15 (S/Fe = 0.5), (d) P-1 wt% FeO$_x$/SBA-15 (P/Fe = 0.5), (e) P-1 wt% FeO$_x$/SBA-15 (P/Fe = 1). (B): (a) 1 wt% FeO$_x$/SBA-15, (b) Cs-1 wt% FeO$_x$/SBA-15 (Cs/Fe = 0.5), (c) Rb-1 wt% FeO$_x$/SBA-15 (Rb/Fe = 0.5), (d) K-1 wt% FeO$_x$/SBA-15 (K/Fe = 0.5), (e) Na-1 wt% FeO$_x$/SBA-15 (Na/Fe = 0.5), (f) Li-1 wt% FeO$_x$/SBA-15 (Li/Fe = 0.5). Reaction conditions: T = 450–650 °C; W = 0.1 g; F = 120 mL min^{-1}; P(CH$_4$) = P(O$_2$) = 33.8 kPa.

1059 cm^{-1} arising from the alternatively connected tetrahedral PO$_4$ and FeO$_4$ groups [18,23]. The FePO$_4$ nanoclusters encapsulated in MCM-41 [18] or SBA-15 [23] also exhibited broadened and overlapped Raman bands as observed here. Therefore, it is reasonable to speculate that FePO$_4$ nanoclusters have been formed over the P-FeO$_x$/SBA-15 sample. The formation of FePO$_4$ nanoclusters containing irons sites surrounded by phosphate groups probably accounts for the best catalytic performances of the P-FeO$_x$/SBA-15 for HCHO formation.

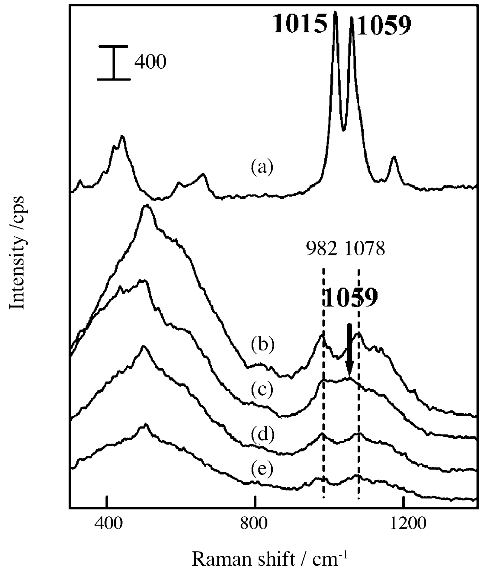

Fig. 4. Raman spectra of the modified FeO$_x$/SBA-15 as well as FePO$_4$. (a) FePO$_4$, (b) 1 wt% FeO$_x$/SBA-15, (c) P-1 wt% FeO$_x$/SBA-15 (P/Fe = 0.5), (d) S-1 wt% FeO$_x$/SBA-15 (S/Fe = 0.5) and (e) B-1 wt% FeO$_x$/SBA-15 (B/Fe = 0.5).

Table 2
Catalytic results for the partial oxidation of CH$_4$ by N$_2$O[a]

Catalyst	CH$_4$ conversion (%)	Selectivity (%)		Oxygenate yield (%)
		CH$_3$OH	HCHO	
0.1 wt% Fe-SBA-15	3.1	2.0	19	0.65
0.1 wt% FeO$_x$/SBA-15	3.0	6.0	26	0.96

[a] Reaction conditions: T = 550 °C; catalyst = 0.05 g; total flow rate = 60 mL min^{-1}; P(CH$_4$) = P(O$_2$) = 16.9 kPa.

3.3. Partial oxidation of CH$_4$ by N$_2$O over the iron-containing SBA-15 catalysts with and without modifications

Table 2 compares the catalytic performances of the Fe-SBA-15 and the FeO$_x$/SBA-15 for the partial oxidation of CH$_4$ by N$_2$O. CH$_3$OH was also formed in addition to HCHO over the two catalysts on this occasion. It is unexpected that the Fe-SBA-15 with tetrahedral iron sites in the framework of SBA-15 gives lower selectivities to CH$_3$OH and HCHO than the FeO$_x$/SBA-15 containing oligomeric FeO$_x$ clusters at a similar CH$_4$ conversion.

The catalytic performances of the 1 wt% FeO$_x$/SBA-15 samples modified by the acid and alkaline additives are shown in Fig. 5. Different from the results obtained using O$_2$ as the oxidant (Fig. 3), most of the additives did not exert significant positive effects on the selectivity to useful oxygenates. Only the P-FeO$_x$/SBA-15 was very unique in producing useful oxygenates including CH$_3$OH and HCHO with a high selectivity. Thus, the FePO$_4$ nanoclusters generated were probably very

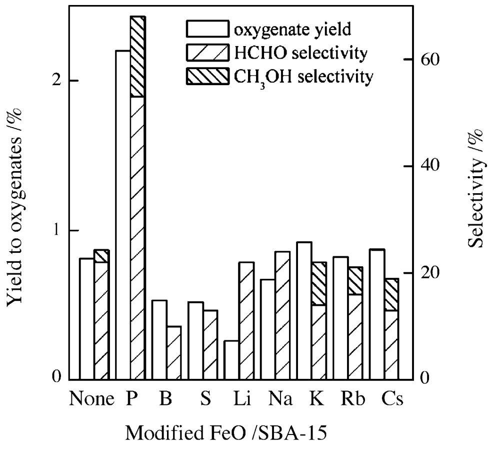

Fig. 5. Catalytic results of the FeO$_x$/SBA-15 modified with various additives for the partial oxidation of CH$_4$ by N$_2$O. Reaction conditions: T = 550 °C; W = 0.05 g; F = 60 mL min^{-1}; P(CH$_4$) = P(N$_2$O) = 16.9 kPa.

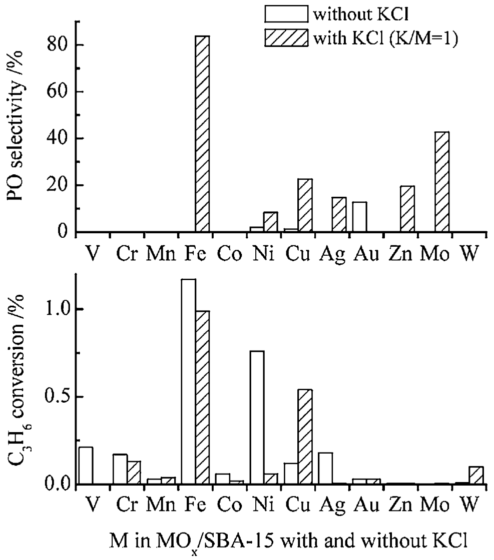

Fig. 6. Catalytic performances of various SBA-15-supported transition metal oxides (MO_x/SBA-15) with and without KCl modification for C_3H_6 oxidation by N_2O. The loading of each metal oxide was 1 wt%, and the K/M (molar ratio) was 1.0. Reaction conditions: $T = 325$ °C; $W = 0.2$ g; $F = 60$ mL min^{-1}; $P(C_3H_6) = 2.53$ kPa; $P(N_2O) = 25.3$ kPa.

special in the activation of N_2O to produce the active oxygen species accounting for the conversion of CH_4 to CH_3OH and HCHO. It is also of interest to note that CH_3OH can also be formed when some alkaline additives are used, and the yield to the oxygenates (CH_3OH and HCHO) is slightly increased after the modification with K^+. Thus, there is also a possibility of the formation of peculiar iron sites capable of activating N_2O in the presence of K^+.

3.4. Requirements for the epoxidation of propylene over iron-containing mesoporous silica

We have found an interesting switching of allylic oxidation to epoxidation during the oxidation of C_3H_6 by N_2O when the FeO_x/SBA-15 catalyst is modified with an alkali metal salt typified by KCl [26]. It is well known that the easy occurrence of the allylic oxidation is the main obstacle for the epoxidation of C_3H_6. Thus, the studies on the chemistry of this system are of high significance. Here we discuss some essential requirements for the occurrence of the epoxidation of propylene over related iron-containing catalysts.

To uncover whether iron is unique for the epoxidation of C_3H_6 by N_2O, we have examined many SBA-15-supported transition metal oxides (1 wt%) with and without KCl modification for this reaction. As shown in Fig. 6, PO was only formed over the 1 wt% Au/SBA-15 with a meaningful selectivity in the absence of KCl modification, but C_3H_6 conversion was very low (<0.1%). The modification with KCl caused the formation of PO over several catalysts. However, the KCl-FeO_x/SBA-15 exhibited remarkably higher PO selectivity (84%) and higher C_3H_6 conversion (1.0%). Thus, iron is peculiar for the epoxidation of C_3H_6 by N_2O.

As described above, the modification of the FeO_x/SBA-15 with phosphate significantly enhanced the formation of CH_3OH and HCHO in the partial oxidation of CH_4 by N_2O (Fig. 5). The P-modified FeO_x/SBA-15 catalyst was also applied for the epoxidation of C_3H_6 by N_2O. However, as shown in Table 3, only a small amount of PO was obtained and the main partial oxidation product was still acrolein over the P-FeO_x/SBA-15. On the other hand, the modification of the FeO_x/SBA-15 with alkali metal salts such as KCl shifted the reaction route from allylic oxidation to epoxidation. The increase in K/Fe ratio from 1 to 5 also increased the C_3H_6 conversion remarkably (Table 3). Thus, the alkali metal salt modifier was vital for PO formation. Using KCl as an example, we have recently clarified that the alkali metal salt plays the following pivotal roles [27]: (1) increasing the dispersion of FeO_x clusters probably via a surface reaction between the finely dispersed FeO_x and KCl; (2) decreasing the reactivity of lattice oxygen associated with the FeO_x and thus suppressing the allylic oxidation; (3) eliminating the surface acidity and thus keeping PO from isomerization.

It is of significance to clarify whether O_2 can be used as an oxidant for C_3H_6 epoxidation over the modified iron-containing catalysts. The catalytic results obtained with O_2 instead of N_2O for the oxidation of C_3H_6 over the 1 wt% FeO_x/SBA-15 with and without KCl modification are also shown in Table 3. Over the 1 wt% FeO_x/SBA-15 without KCl modification, a higher C_3H_6 conversion was obtained with O_2, but the selectivity to the main partial oxidation product, i.e., acrolein became lower as compared with that with N_2O. Unexpectedly, the modification of the FeO_x/SBA-15 with KCl remarkably decreased the C_3H_6 conversion, and the KCl-FeO_x/SBA-15 (K/Fe = 5) was almost

Table 3
Selective oxidation of propylene over the 1 wt% FeO_x/SBA-15 with and without modifications[a]

Catalyst	Oxidant	C_3H_6 conversion (%)	Selectivity (%)[b]			
			PO	Acrolein	Allyl alcohol	CO_x
SBA-15 or K^+-SBA-15 (K/Si = 0.04)	N_2O	0	–			
1 wt% FeO_x/SBA-15	N_2O	1.2	0	42	4.5	46
P-1 wt% FeO_x/SBA-15 (P/Fe = 1)	N_2O	1.4	0.7	64	6.0	16
KCl-1 wt% FeO_x/SBA-15 (K/Fe = 1)	N_2O	1.0	84	2.8	2.2	7.9
KCl-1 wt% FeO_x/SBA-15 (K/Fe = 5)	N_2O	4.5	72	1.6	1.0	18
1 wt% FeO_x/SBA-15	O_2	7.9	1.0	8.0	2.3	87
KCl-1 wt% FeO_x/SBA-15 (K/Fe = 5)	O_2	0.23	2.7	6.5	1.4	88

[a] Reaction conditions: $T = 325$ °C; catalyst = 0.2 g; total flow rate = 60 mL min^{-1}; $P(C_3H_6) = 2.53$ kPa; $P(N_2O) = 25.3$ kPa or $P(O_2) = 12.7$ kPa.

[b] Other products not shown here were acetone, propionaldehyde and acetaldehyde.

inactive for the conversion of C_3H_6 by O_2. Moreover, the selectivity to PO was not significantly enhanced. Therefore, the modified FeO_x/SBA-15 could not function as a useful C_3H_6 epoxidation catalyst when O_2 was used to replace N_2O. In other words, for the iron-catalyzed C_3H_6 epoxidation, the use of N_2O oxidant combined with an appropriately modified active iron site is indispensable.

3.5. Comparisons between O_2 and N_2O as oxidant for partial oxidation of CH_4 and epoxidation of C_3H_6

As described above, significant differences were observed in catalytic behaviors when a different oxidant (i.e., O_2 or N_2O) was used for the partial oxidation of CH_4 or the epoxidation of C_3H_6 over iron-containing heterogeneous catalysts. The elucidation of the nature of such differences may be helpful for the design of a highly active and selective catalytic system. Here we make a preliminary discussion on this issue on the basis of our current results and the known facts.

For the partial oxidation of CH_4 with O_2, HCHO was the only partial oxidation product and no CH_3OH could be detected over our iron-containing catalysts. It was revealed that the higher dispersion of iron species would result in higher HCHO selectivity. For examples, the isolated iron sites in the framework of a mesoporous silica were better than the FeO_x clusters; both the acid and alkaline additives enhanced HCHO selectivity because of the increased dispersion of iron species in the presence of these additives although the environment of iron also affected the catalytic performances. When N_2O was used for the partial oxidation of CH_4 over our iron-containing catalysts, CH_3OH was also formed in addition to HCHO. On the basis of our previous comparative studies on the partial oxidation of CH_4 over MCM-41-supported $FePO_4$ catalysts [18], we propose that, different from the case using O_2 where a redox mechanism via lattice oxygen is responsible for the conversion of CH_4 to HCHO, a special adsorbed active oxygen generated on a special iron site accounts for the conversion of CH_4 to CH_3OH and HCHO using N_2O. In the latter case, the FeO_x clusters located on the wall surface of a mesoporous silica worked more efficiently than the framework iron sites. For the oxidation of benzene to phenol with N_2O catalyzed by the Fe-ZSM-5, it is generally accepted that the extraframework iron is responsible for the activation of N_2O [28,29]. It is thus possible that the framework iron sites are difficult to activate N_2O to generate the peculiar active oxygen species although we do not know whether the active oxygen species in our case resembles that for benzene to phenol. Moreover, among many modified FeO_x/SBA-15 catalysts, only the P-FeO_x/SBA-15 exhibited uniquely higher selectivity and yield to CH_3OH and HCHO in the case of using N_2O. We speculate that the $FePO_4$ nanoclusters formed in the mesopores of SBA-15 are very unique for the activation of N_2O to the special active oxygen species. The K-FeO_x/SBA-15 also enhanced the formation of CH_3OH in the case of using N_2O.

For the oxidation of C_3H_6, PO could not be formed or was only a minor product when O_2 was used over any of our iron-containing catalysts. The allylic oxidation by nucleophilic oxygen species (lattice oxygen) must proceed rapidly in the presence of O_2. On the other hand, by using N_2O, PO could be obtained with high selectivities (>70%) over an appropriately modified iron-containing catalyst. We can expect that the activation of N_2O may generate a special oxygen species with electrophilic characteristic on the iron site. However, the modification with an alkali metal salt typified by KCl is necessary for the formation of the active iron sites. Further elucidations of the active iron sites and the active oxygen species are still needed in future studies.

4. Conclusions

The location, dispersion and environment (acidic or alkaline) of iron sites and the nature of oxidant are key factors in determining the catalytic performances of iron-containing mesoporous materials for selective oxidation reactions. For the partial oxidation of CH_4 by O_2, a higher dispersion of iron sites is required for obtaining a higher selectivity to HCHO. The alkaline is detrimental to HCHO selectivity. On the other hand, HCHO selectivity can be remarkably enhanced by the formation of $FePO_4$ clusters, in which the tetrahedral iron sites are surrounded by the acidic phosphate groups. In the case of CH_4 oxidation by N_2O, the catalyst with $FePO_4$ clusters is unique in achieving high selectivity to CH_3OH and HCHO. The location of iron is vital in the case of using N_2O, and the catalyst containing framework iron exhibits poorer catalytic performances for the oxidation of CH_4 to CH_3OH and HCHO. The use of N_2O oxidant is necessary for the epoxidation of C_3H_6 over the iron-containing catalysts. Iron is peculiar for obtaining high selectivities to PO, and the modification of the iron sites with an alkali metal salt is also required for the occurrence of C_3H_6 epoxidation.

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