

Synthesis, characterization and catalytic performance of metal-incorporated SAPO-34 for chloromethane transformation to light olefins

Yingxu Wei^a, Dazhi Zhang^a, Lei Xu^a, Fuxiang Chang^a,
Yanli He^a, Shuanghe Meng^a, Bao-lian Su^{b,**}, Zhongmin Liu^{a,*}

^aApplied Catalysis Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, PR China

^bLaboratoire de Chimie des Matériaux Inorganiques, The University of Namur (FUNDP), 61 rue de Bruxelles, B-5000 Namur, Belgium

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Abstract

SAPO-34 and MeAPSO-34s (Me=Co, Mn, Fe) molecular sieves have been synthesized and used as catalysts for chloromethane transformation to light olefins. The influences created by metal incorporation are characterized with XRD, XRF, SEM, NMR, TG and H₂-TPR. The synthesized MeAPSO-34s have the same CHA topology structure, while metal incorporation gives rise to the increase of unit cell parameter and crystalline particle size. The coexistence of metal species in the synthesis starting gel has effect on the Si substitution into AlPO framework. Co, Mn or Fe incorporation generates a negligible difference on the chemical shift in ³¹P and ²⁷Al MAS NMR. ²⁹Si MAS NMR study has demonstrated that metal incorporation favors the Si island formation, predicting the stronger acidity. The reducibility of metal species in the synthesized MeAPSO-34s has been investigated by H₂-TPR with the comparison of metal-impregnated SAPO-34. Two weight losses in TG analysis from template decomposition in diluted oxygen suggest different chemical location of template molecules in the molecular sieves. For MeAPSO-34, more template removal occurrence at high temperature range indicates stronger template-framework interaction and stronger acidity than SAPO-34 after calcinations. All the SAPO-34 and MeAPSO-34 molecular sieves are very active and selective catalyst for light olefins production. Metal incorporation improves the catalyst life and favors the ethylene and propylene generation. These catalytic properties enhancements are possibly related to the mechanism of chloromethane conversion with deposited coke species as reaction center.

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1. Introduction

Aluminophosphate (AlPOs) and silicoaluminophosphate (SAPOs) molecular sieves, a type of microporous materials with P-Al or Si-P-Al framework, have been widely used as shape-selective catalysts in many processes [1–3]. Among SAPO molecular sieves, small pore SAPO-34 exhibits particularly high ethylene and propylene selectivity in MTO process [4]. Many elements have been incorporated into SAPO-34 framework by isomorphous substitution to form MeAPSOs

molecular sieves (Me=Be, B, Mg, Ti, Mn, Fe, Co, Ni, etc.) [5,6]. With these modification, MeAPSO-34 showed improved light olefins selectivity in MTO process, such as Ni incorporation gave rise to extremely high ethylene selectivity of 90% and over SrAPSO-34, ethylene and propylene selectivity attained to 89.5% [7,8].

With the application of SAPOs and MeAPSOs in a series of catalytic processes [9–11], the effect of metal incorporation on framework element coordination and acid sites formation have been also studied. SAPO framework consists of tetrahedral Al, P and Si species. With metal incorporation, metal substitutes the Al³⁺ site in the framework to form P(*n*Al, (4 – *n*)Me) chemical environments [12–14]. The work of Ashtekar et al. and our recent study indicated that metal incorporation into SAPO framework would influence the Si coordination states [15]. Akporiaye et al. proposed that in the MgAPSOs, the only likely site for silicon

* Corresponding author. Tel.: +86 411 84685510; fax: +86 411 84691570.

** Corresponding author. Tel.: +32 81 724531; fax: +32 81 725414.

E-mail addresses: bao-lian.su@fundp.ac.be (B.-l. Su),
liuzm@dicp.ac.cn (Z. Liu).

incorporation was the P(4Al) site [16]. Si incorporation is the key for acid site formation of SAPO molecular sieves. These observations mentioned above predict the acidity and catalysis difference of MeAPSO from SAPO molecular sieves, while the correlation between metal substitution into SAPO framework with catalytic property improvement is still not very conclusive. Clarifying the influence caused by metal incorporation and corresponding change in catalytic performance has been the motivation of this study.

In the present work, SAPO-34 and MeAPSO-34 (Me=Co, Mn, Fe) have been synthesized with hydrothermal method. The differences in crystalline, morphology and framework element coordination states caused by metal incorporation are studied by XRD, SEM and NMR. The reducibility of transition metal (Co, Mn and Fe) in MeAPSO-34 framework is determined by H_2 -TPR with the comparison of metal-impregnated SAPO-34. The removal of template molecular occluded in the CHA cage is evaluated with thermal analysis and the difference of template location in SAPO-34 and MeAPSO-34 has been discussed.

Previous study has proved that SAPO-34 and MeAPSO-34 are excellent catalyst for light olefins production from methanol transformation [17,18]. Our recent work and the work of Svelle et al. indicate that SAPO-34, beside its successful application in MTO process, are also very potential catalyst for the process of chloromethane transformation to light olefins, an alternative route for natural gas utilization with halogenated methane as intermediates [19–22]. This process was first proposed by Olah et al. [23] and zeolite catalysts, such as ZSM-5, Y and MOR, were usually employed as catalysts in the previous study [24–29]. Chloromethane has been mainly transferred to light alkanes and higher hydrocarbon products in gasoline range over zeolite catalysts [24,25]. The performance for light olefins production catalyzed by zeolite catalysts was less satisfactory. Using SAPO molecular sieves with mild acidity and small pore opening as catalysts made it possible for highly efficient chloromethane conversion to light olefins products [19,22]. SAPO-34 and MnAPSO-34 have been proved to be very potential catalyst in chloromethane conversion to light olefins [20]. Therefore, in the present work, beside the study of metal incorporation into SAPO framework, we also try to develop new MeAPSO-34 catalysts (Me=Co, Mn, Fe) for chloromethane transformation to light olefins with variable and improved performances.

2. Experimental

2.1. Synthesis

The synthesis of SAPO-34 and MeAPSO-34s (Me=Co, Mn, Fe) followed the procedure reported in the literature [20,30]. Pseudoboehmite, orthophosphoric acid, colloidal silica, $Co(CH_3COO)_2 \cdot 4H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were used as the sources of aluminum, phosphorus, silicon, cobalt, manganese and iron, respectively. Triethylamine (TEA) was used as the template. The chemical composition of the starting gel was $1.0Al_2O_3:1.0P_2O_5:0.8SiO_2:3.0TEA:50H_2O$

for SAPO-34 and $1.0Al_2O_3:1.0P_2O_5:0.8SiO_2:0.05MeO_x:3.0TEA:50H_2O$ for MeAPSO-34. The gels were sealed in the stainless-steel autoclave lined with polytetrafluoroethylene (PTFE) and the autoclave was heated at 200 °C for 15 h under autogeneous pressure. The products were filtrated, washed, and dried at 110 °C for 3 h.

The Co, Mn or Fe-impregnated SAPO-34 were prepared by impregnation method with the solution of $Co(CH_3COO)_2 \cdot 4H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$ containing the same amount of metal species as MeAPSO-34s (Me=Co, Mn or Fe), respectively.

2.2. Characterizations

2.2.1. Crystallinity, morphology and coordination states

The crystallinity and the phase purity of the as-synthesized samples were analyzed by powder X-ray diffraction (RIGAKU D/max-rb powder diffractometer) with Cu K α radiation. The chemical composition of the samples was determined with Bruker SRS-3400 XRF spectrometer. Scan electron microscope (SEM) images were obtained on a KYKY-1000 instrument operated at 25 kV. ^{31}P , ^{27}Al and ^{29}Si MAS NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer.

2.2.2. H_2 -TPR

H_2 -TPR was performed using a chemical adsorption unit (Micrometric Autochem 2910). The samples were pretreated in He flow at 650 °C for 30 min and then the temperature was adjusted to 50 °C. The sample was heated from 50 to 900 °C with a heating rate of 10 °C/min under the atmosphere of hydrogen and helium ($H_2/He = 10$). The temperature-programmed reduction products were analyzed in situ with Omnistar mass spectrometer (Balzers).

2.2.3. Template removal

The template decomposition in diluted oxygen (2% O_2 in Ar) was performed using TA TGA2950. The sample was heated from 50 to 800 °C with a heating rate of 10 °C/min.

2.3. Chloromethane conversion

2.3.1. Catalytic performance

The catalytic tests were performed using a fixed bed reactor system at atmosphere pressure. 0.62 g of catalyst was loaded into a quartz reactor with an inner diameter of 5 mm. The sample was pretreated in a flow of dry nitrogen at 500 °C for 1 h and then the temperature of reactor was adjusted to 450 °C and the atmosphere was replaced by nitrogen and chloromethane (the molar ratio of N_2/CH_3Cl was 1). The weight hourly space velocity (WHSV) was $3.2 h^{-1}$ for chloromethane. The product stream was kept at 180 °C and analyzed on-line by a Varian GC3800 gas chromatograph equipped with a FID detector and a PONA capillary column.

2.3.2. Coke formation studied by thermal analysis

The coke deposition of the catalysts after reaction was analyzed by TG-DSC method. An amount of 10–15 mg of

discharged catalyst was loaded in the crucible of the microbalance. The temperature was increased from room temperature to 800 °C at a rate of 5 °C/min under dry air flow. The weight loss and calorimetric effect were recorded.

3. Results and discussion

3.1. Synthesis

3.1.1. Crystalline structure, morphological features and chemical composition

The XRD patterns of the as-synthesized SAPO-34 and MeAPSO-34 (Me=Co, Mn, Fe) molecular sieves show that the position and the intensity of the diffraction peaks of all the samples are identical to those reported in the literature [20], so they are not given in the present work. The bulk chemical compositions of the calcined SAPO-34 and MeAPSO-34 are detailed in Table 1. For clear comparison of framework element substitution, the synthesis of SAPO-34 and MeAPSO-34s is from the starting gel with the same Al:P:Si ratio and using the same template of triethylamine, just introducing a certain amount of metal species to the gel, while the chemical compositions of the synthesized samples imply that the coexistence of metal ions in the starting gel has effect on the Si substitution into AlPO frameworks. Actually, among the five samples, SAPO-34 has the highest Si content. With metal incorporation, Si incorporation decreases. The unit cell parameters of synthesized samples are calculated with resolving SAPO-34 and MeAPSO-34 as hexagonal cell and the results are listed in Table 1. The increase of unit cell parameter with Co or Mn incorporation proves the substitution of metals into the framework. All the synthesized MeAPSO-34 samples have cubic morphology as shown in SEM photos (Fig. 1), noting that the size of metal-incorporated SAPO-34 crystals are a little bit larger.

3.1.2. ^{31}P , ^{27}Al and ^{29}Si MAS NMR spectra

SAPO-34 and MeAPSO-34s give very similar ^{31}P and ^{27}Al MAS NMR spectra and the attributions of the signals have been given in our previous study [20], so they are not presented here. Fig. 2 shows the ^{29}Si MAS NMR spectra of SAPO-34 and MeAPSO-34s. Five resonance signals appear in the spectra. The signals with chemical shift of -91.3 and -95.0 ppm, stemming from the coordination states of Si(4Al) and Si(3Al), respectively, show relatively high intensity. The signals at -100.3 , -104.8 and -109.2 , originated from the coordination states of Si(2Al), Si(1Al) and Si(0Al), respectively, present

relatively low intensity. It is easy to observe that, for the metal-incorporated samples, the signal at -109.2 ppm from Si(0Al) species is more prominent in intensity than that of SAPO-34, indicating that more Si islands may appear in the metal-incorporated SAPO framework. This phenomena has been observed in Mn-incorporated SAPO-34 [20] and in this study, it is also proved by the spectra of Co and Fe-containing samples.

3.2. H_2 -TPR profiles

Metal incorporation with isomorphous substitution is the key for the synthesis of metal-containing SAPO molecular sieves. Whether metal species was incorporated into the framework of the molecular sieve or it was just dispersed over the surface? This needs to be confirmed by means of certain characterization methods. It is easy to speculate that transition metal species in different chemical environments will give rise to the difference in the reduction properties of the metal species. For comparison, metal oxides-supported SAPO-34 (Me=Mn, Co, Fe) were also prepared with impregnation method. The H_2 -TPR profiles of the synthesized and impregnated SAPO-34 containing Mn, Co and Fe species are depicted in Fig. 3.

For the impregnated samples of Co-SAPO-34 (Fig. 3A-b), a reduction peak appears clearly in the temperature range of 300–450 °C, indicating that some impregnated cobalt oxide can be reduced at this temperature. However, for the hydrothermally synthesized sample of CoAPSO-34 (Fig. 3A-a), its reduction peak appears at 700–850 °C. The TPR profiles of Mn and Fe-containing SAPO-34 also indicate that the supported Mn species and Fe species could be reduced at temperature lower than 700 °C, while for synthesized MnAPSO-34 and FeAPSO-34, no metal species reduction occurs even until 900 °C. Usually the reducibility of metal species is closely related with its chemical environment [11]. The difficulty in reducing the metal species of MeAPSO-34 implies that the chemical environment of the metal species introduced by hydrothermal synthesis is not same as the metal species of supported metal oxides. The metal atoms in MeAPSO-34s are more possibly incorporated into the framework. Strong bonding with other framework elements causes the reduction more difficult to be realized.

3.3. Template removal

Template decomposition of as-synthesized SAPO-34 and MeAPSO-34s in diluted oxygen flow was analyzed by TG

Table 1
Chemical composition and unit cell parameters of the as-synthesized SAPO-34 and MeAPSO-34s

Sample	Chemical composition (in mole)	Unit cell parameters		
		$a = b$ (Å)	c (Å)	V (Å ³)
SAPO-34	$\text{Al}_{0.483}\text{P}_{0.410}\text{Si}_{0.107}\text{O}_2$	13.80	14.92	2462.50
CoAPSO-34	$\text{Co}_{0.020}\text{Al}_{0.466}\text{P}_{0.421}\text{Si}_{0.093}\text{O}_2$	13.89	14.99	2505.33
MnAPSO-34	$\text{Mn}_{0.020}\text{Al}_{0.476}\text{P}_{0.412}\text{Si}_{0.092}\text{O}_2$	13.93	15.06	2530.03
FeAPSO-34	$\text{Fe}_{0.014}\text{Al}_{0.476}\text{P}_{0.410}\text{Si}_{0.099}\text{O}_2$	13.80	14.92	2459.62

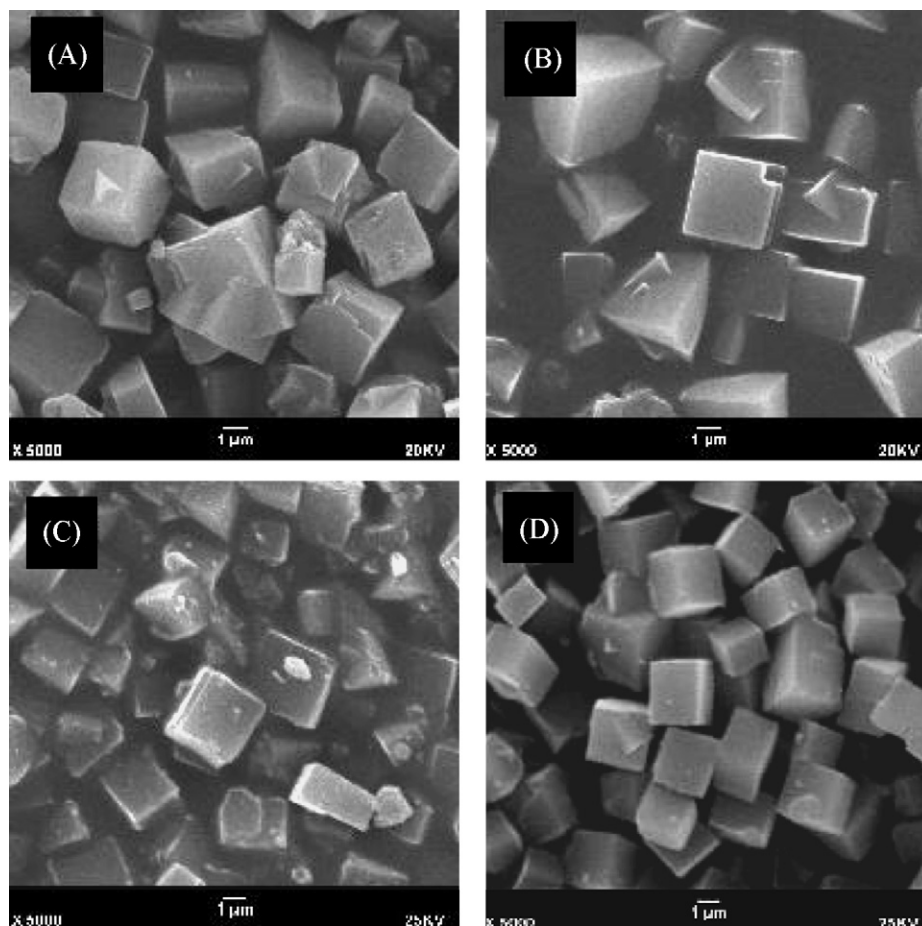


Fig. 1. Scanning electron micrographs of as-synthesized MeAPSO-34 (Me=Co (A), Mn (B), Fe (C) and SAPO-34 (D)).

method and the results are compared in Fig. 4 and Table 2. The weight loss in the range of 25–200 °C should be attributed to the water desorption from the samples. The very steep weight loss (I) in the range of 200–440 °C and another relatively gradual

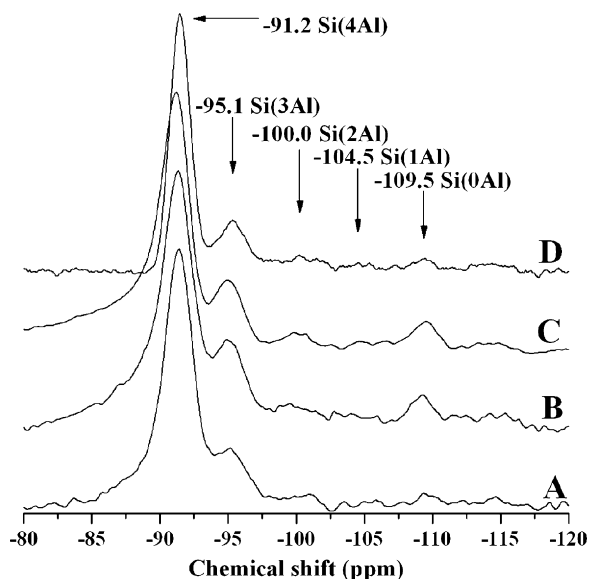


Fig. 2. The ^{29}Si MAS NMR of as-synthesized MeAPSO-34 (Me=Co (A), Mn (B), Fe (C) and SAPO-34 (D)).

weight loss (II) in the range of 440–700 °C correspond to the decomposition of organic template, triethylamine [20]. Previous study indicated that the weight loss due to the template removal of some zeolites could occur in different temperature range [31–35]. For ZSM-5 zeolite with TEOH as the synthesis template, two weight losses around 250 and 480 °C are assigned to the removal of TEOH occluded in the zeolite and TEA^+ associated with $(\text{Si}-\text{O}-\text{Al})^-$ group, respectively [32]. In the present study, triethylamine is structure-directing agent for SAPO-34 and MeAPSO-34s synthesis. On the other hand, template molecular also acts as a charge compensator for the negatively charged lattice of SAPO and MeAPSOs [34,36]. Usually, the protonated amine template for charge balance is more difficult to be removed than neutral template occluded in the channel, which is explained by the strong template-framework interaction between protonated template and negatively charged framework [36]. The two-stage template degradation presented in Fig. 4 should be attributed to the removal of neutral template molecular and charged template molecular in the channel of as-synthesized molecular sieves.

Template removal is associated with OH generation, so the template degradation temperature may predict the Brönsted acidity strength [31]. Detailed TG results listed in Table 2 indicates that even though the weight losses are in roughly the same temperature range for all the synthesized samples, the

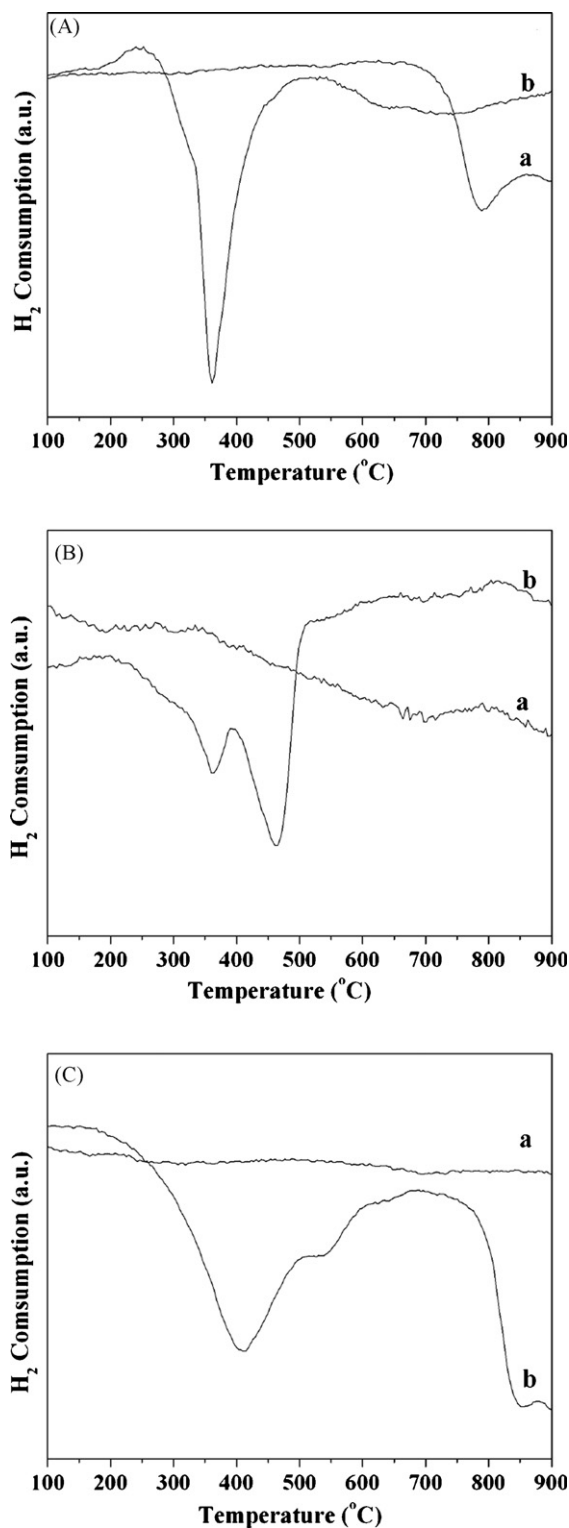


Fig. 3. H_2 -TPR profiles of Co (A), Mn (B) or Fe (C) containing SAPO-34. (a) Synthesized MeAPSO-34, (b) metal-impregnated SAPO-34.

proportion of weight loss in the two template removal stages is different. For SAPO-34, the weight losses related to template removal is 77.37% for stage I and 22.63% for stage II, while for MeAPSO-34 (Me=Co, Mn, Fe), the proportion of weight loss at higher temperature range (stage II) attained to 31.80, 46.51 and 23.31%, respectively, meaning that the quantity of template

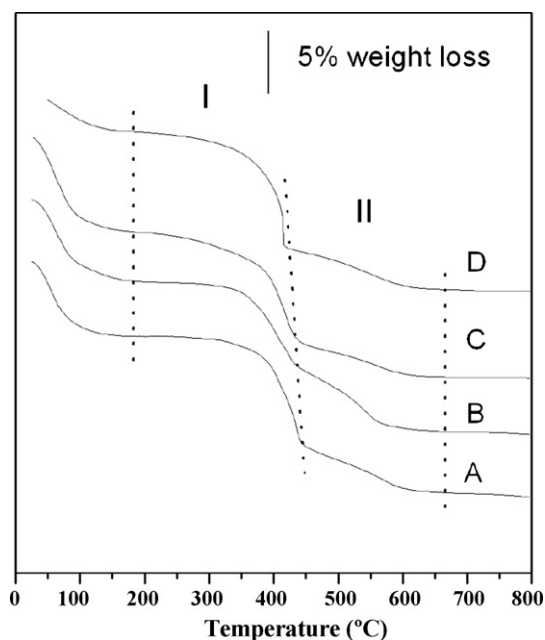


Fig. 4. Template removal of as-synthesized MeAPSO-34 (Me=Co (A), Mn (B), Fe (C) and SAPO-34 (D)).

molecular in this chemical environment is higher than SAPO-34, especially in CoAPSO-34 and MnAPSO-34. For MeAPSOs, the isomorphous replacement of P^{5+} by Si^{4+} or Al^{3+} by bivalent metal ions Me^{2+} generates negatively charged framework. At the same time, no metal cations, such as Na^+ , exist in the channel, so the negative charge of the framework will be balanced by protonated template. After the removal of the template with calcination, protons will be left attached to the framework oxygen for charge compensation, so in this way, Brönsted acid sites form simultaneously. The different weight loss percentage in stages I and II observed in SAPO-34 and MeAPSO-34s suggests clearly the stronger template-framework interaction between template molecular of TEA and MeAPSO-34 framework. After the removal of the template, stronger acidity may generate correspondingly.

The average number of template molecular in each CHA-cage is evaluated with the total weight loss from template removal, combining with the crystalline chemical composition given in Table 1. This value shows a slight increase with Mn and Co incorporation. This may stem from the enlarged cage volume which has been discussed in Section 3.1.1.

3.4. Chloromethane conversion over SAPO-34 and MeAPSO-34s

3.4.1. Catalytic test

Catalytic transformation of chloromethane was performed over SAPO-34 and MeAPSO-34s. The evolution of conversion and product selectivity as a function of reaction time are given in Fig. 5. At the beginning of the transformation with reaction time of 5 min, all the catalysts, SAPO-34 and MeAPSO-34s present high CH_3Cl conversion indicating their high initial activity. The conversions over MeAPSO-34 (Me=Co, Mn, Fe) are slightly higher than SAPO-34. Prolonging the reaction time, all the five

Table 2

Template occlusion in the CHA cage and detailed template removal stages

	Sample			
	CoAPSO-34	MnAPSO-34	FeAPSO-34	SAPO-34
Percent of template in samples (wt%)	13.42	12.90	12.67	12.53
Template molecular/cage	1.11	1.06	1.04	1.02
Template removal stage I				
Temperature (°C)	245–445	245–430	200–445	230–445
Weight loss (wt%)	68.20	53.49	76.69	77.37
Template removal stage II				
Temperature (°C)	445–720	430–720	445–720	410–700
Weight loss (wt%)	31.80	46.51	23.31	22.63

catalysts lose their activity with time on stream. While it is easy to observe that for Co, Mn or Fe incorporated samples, their conversion decrease is remarkably slower than that of SAPO-34, implying that metal incorporation into SAPO-34 framework is helpful to keep the catalytic activity and prolong the catalyst life. This improvement in catalyst life should be related to acidity modification by metal incorporation.

Detailed product distribution given in Fig. 5 shows that over synthesized SAPO-34 and metal incorporated SAPO-34 catalysts, light olefins could be produced with very high selectivity. Ethylene, propylene and butenes are prominent among the products. Light alkanes (C_1 – C_4 alkanes) selectivity

is relatively low. This is quite different from zeolite-catalyzed chloromethane transformation with aromatics and paraffins as main products [24–27]. In this study, metal incorporation into SAPO-34 presents mild modification effect on the catalytic performance. For Mn, Co, Fe-containing SAPO-34, beside their slightly enhancement of CH_3Cl conversion, it is worthy to note metal incorporation also varies the product distribution. Among the light olefins products, Co and Fe incorporation favors the ethylene production and Mn and Fe incorporation is helpful for propylene generation. Over SAPO-34 catalyst, butenes are more predominant formed, while butenes generation could be depressed with using FeAPSO-34 as catalyst.

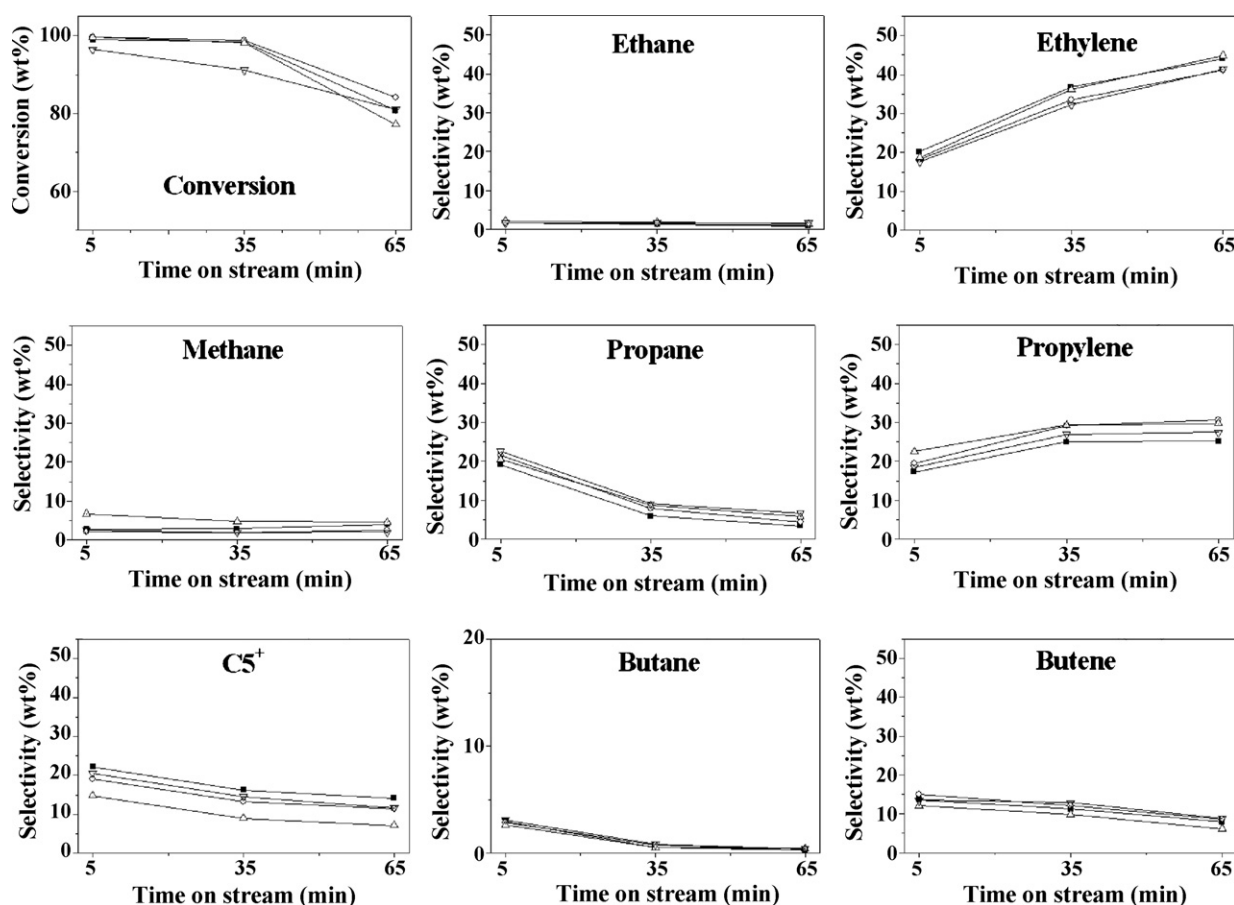


Fig. 5. Catalytic performance of chloromethane transformation over CoAPSO-34 (■), MnAPSO-34 (○), FeAPSO-34 (△) and SAPO-34 (▽).

Product selectivity changes with time on stream. At the reaction time of 5 min, Propylene and ethylene generate in relative low selectivity. Prolonging the reaction time, light olefins become main products. Ethylene selectivity increases gradually and attains to about 40 wt% for all the studied catalysts. Propylene selectivity shows an increase in the beginning 35 min and keeps stable at 20–30 wt%. Butenes selectivity goes through a slight increase and then decreases slowly. These light olefins selectivity evolutions with reaction time should be attributed to the modification of the catalyst pore opening by coke disposition during chloromethane transformation. With the production of a large amount of light olefins, alkanes products, such as methane, ethane, propane, butanes and the products large than C5 (C5⁺), generate with low selectivity. HCl is also observed in the products, but is not listed in the product distribution.

3.4.2. Coke formation

Coke amount of the discharged catalyst SAPO-34, CoAPSO-34 and MnAPSO-34 were analyzed by TG and the curves are compared in Fig. 6. Two weight losses (I and II) appear in the TG curves. The first weight loss (I) in the range of

25–200 °C with endothermic effect is from water desorption. The second weight loss (II) in the range of 200–550 °C with exothermic effect corresponds to the coke calcination. The combustion of the coke species occurs in the same temperature range, while their coke amounts are different. The weight loss from coke calcination of SAPO-34 is 10.26 wt%, while this value is 10.40 wt% for CoAPSO-34 and 10.55 wt% for MnAPSO-34, slightly higher than SAPO-34.

Coke formation is from the second reaction of the products of light olefins, such as oligomerization and hydrogen transfer, which are correlated with the strength and amount of acid site over the catalyst surface. The ²⁹Si MAS NMR spectra (Fig. 2) and the result of template removal (Fig. 4) give the information that metal incorporation brings about stronger acidity. This could explain the relatively high chloromethane conversion and more coke deposition over MnAPSO-34 and CoAPSO-34.

Coke formation from second reaction of light olefins will consume the light olefins products and alkanes products generate at the same time. While in the present study, both coke formation and ethylene and propylene production are favored by Co or Mn modified catalysts. Previous study of chloromethane conversion to higher hydrocarbons employed hydrocarbon-pool mechanism to explain the light olefins generation over catalyst surface [19,28]. In the present study, higher conversion over MeAPSO-34 may stem from its relatively more hydrogen-deficient species deposited in the CHA cage, which behaves as reaction center for light olefins production [37,38].

4. Conclusion

MeAPSO-34s (Me=Mn, Co, Fe) were synthesized and presented same CHA crystalline structure and cubic morphology as SAPO-34. During the synthesis, the coexistence of metal species in starting gel suppressed Si incorporation into framework and varied the Si coordination states. The increased unit cell parameters from XRD and special reducibility of incorporated Co, Mn and Fe evidenced by H₂-TPR clearly proved the isomorphous substitution of metal species into SAPO framework. More template degradation occurrence at high temperature from Co or Mn containing SAPO-34 than SAPO-34 and more Si island formation predicted strong acid sites generation with metal incorporation. Metal incorporation also modified the catalytic performance of SAPO-34. The application of MeAPSO-34s in chloromethane transformation brought about more stable catalytic activity and improved light olefins production. Ethylene production is favored using Co or Fe incorporated catalysts and propylene generation is more predominant over Mn or Fe-containing SAPO-34s. Slightly more coke deposition was employed to explain the higher chloromethane conversion and enhanced light olefins production using MeAPSO-34s as catalysts.

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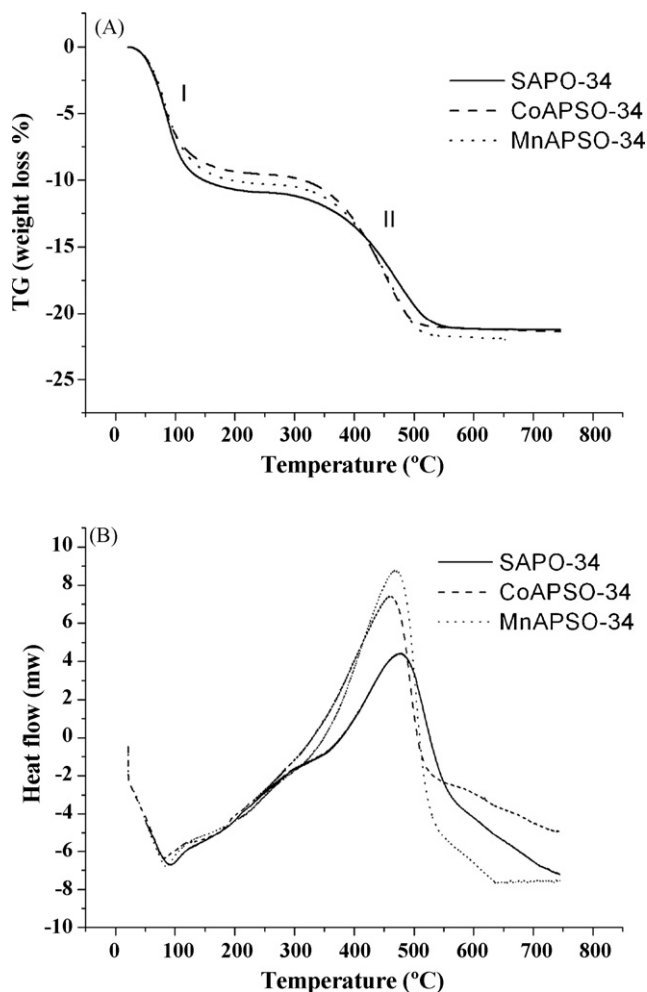


Fig. 6. Thermal analysis of discharged SAPO-34, CoAPSO-34 and MnAPSO-34 ((A) TG and (B) DSC).

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