Incorporation of mixed metals into SAPO-34 frameworks by the dry-gel conversion method using mixed templates: investigating catalysts characterisation and performance

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ABSTRACT
The crystallisation of the MeAPSO-34 material was studied under dry-gel conversion conditions and using two and three templates. This study has been focused on the effect of the incorporation of a mixture of Ni and Mn into the SAPO-34 framework. The MeSAPO-34 samples were characterised by X-ray diffraction, energy-dispersive X-ray spectrometer, scanning electron microscope, temperature-programmed desorption and Brunner–Emmett–Teller. The influence of metal incorporation into the framework of SAPO-34 (MeAPSO-34) on methanol conversion was investigated in this study. The performances on methanol conversion for these catalysts were different according to the properties of metals incorporated into the SAPO-34 structure. The catalytic performance demonstrated high activity and light olefins selectivity for the prepared catalysts. Among the light olefin products, Mn and Ni incorporation is helpful for propylene generation, but samples with a mixture of Ni and Mn favour the ethylene production.

KEYWORDS
metal incorporation; nanoparticles; DGC method; MTO reaction; mixed templates

1. Introduction
Methanol-to-olefins (MTO) process has proven to be the most successful way to produce ethylene and propylene.[1] The SAPO-34 molecular sieve with chabazite (CHA) structure has exhibited excellent performance as a membrane or adsorbent in sorption reactions and catalyst in MTO reaction.[2] The characteristics of SAPO-34 or its modification and its applications in the MTO process have been described elsewhere.[3]

The isomorphous substitution of aluminium atoms by transition metal atoms (like Fe, Ni, Co and Mn) can form P(nAl, (4 – n)Me) chemical environments and would influence the Si coordination states.[4,5] Kang reported that the selectivity to ethylene increased on metal-incorporated catalysts compared with the non-metal catalyst.[6] However, results are not always similar. For example, some investigations have reported significantly
higher ethylene selectivity for NiAPSO-34; [7] while other investigations have reported NiAPSO-34 leads to less production of ethylene.[8]

A different synthetic method, namely dry-gel conversion (DGC), was introduced a few years ago as an alternative to hydrothermal synthesis (HTS) method.[9] In this method, before crystallisation the initial gel is dried up at elevated temperature and atmospheric pressure. Unlike HTS, DGC has several advantages; for example, we can mention minimum waste disposal, reduced reactor size, reduced consumption of the template, the possibility of continuous production of porous materials, etc. Moreover, it has been suggested that DGC may be useful to produce a porous material from pre-shaped gels. The lack of the liquid phase may result in limited mass transport, and therefore lower crystal growth rates.[10]

In this sense, the aim of this paper is to analyse catalytic performances in the MTO reaction of different SAPO-34 samples prepared by the DGC method in the presence of mixed templates and different metals (Ni, Mn and a mixture of Ni and Mn) incorporated in the solid samples.

Vomscheid et al. [11] indicated that the importance of the template appears not only in its role of directing the structure, but also about controlling the distribution of Si in the framework, which clearly affects the catalytic properties of the samples. Najafi et al.[12] reported that in the case of samples, which were synthesised with DEA (diethylamine) and morpholine as templates, the typical cubic-like rhombohedra morphology is obtained.

2. Experimental

2.1. Catalyst preparation

In this study, MeAPSO-34 samples were synthesised by a DGC method. Molar ratios of compositions in the gel mixture and used metal ions are described in Table 1. The MeSAPO-34 molecular sieves were synthesised using aluminium isopropoxide Al(OPri)₃ (Merck), phosphoric acid (85 wt%, Merck), tetraethyl orthosilicate (TEOS, Merck) and distilled water. Morpohline (Merck), DEA (Merck) and triethylamine (TEA, Merck) were used as structure-directing agents. Nickel sulphate (NiSO₄·6H₂O, Merck) and manganese chloride (MnCl₂·4H₂O, Merck) are the source of the metals. The synthesis solution (containing the source of materials and templates with mentioned ratios in Table 1) was stirred and then dried at the high temperature (about 80−100 °C) to give a viscous gel. The dried gel was placed in a Teflon-lined stainless steel vessel and a small amount of water that served as a source of steam was separately added to the same vessel. Crystallisation was conducted for 6 h. The products were rinsed with deionised water and finally calcined for 5 h at 500 °C.

| Catalyst | Synthesis gel composition (molar basis) | Metal |
|----------|----------------------------------|-------|
| S-1      | Al₂O₃: 1.0 P₂O₅: 3.0 morpholine:1 DEA: 0.6 SiO₂: 0.05 MeO: 70 H₂O | Ni    |
| S-2      | Al₂O₃: 1.0 P₂O₅: 3.0 morpholine:1 DEA: 0.6 SiO₂: 0.1 MeO: 70 H₂O | Ni    |
| S-3      | Al₂O₃: 1.0 P₂O₅: 3.0 morpholine:1 DEA: 0.6 SiO₂: 0.05 MeO: 70 H₂O | Mn    |
| S-4      | Al₂O₃: 1.0 P₂O₅: 3.0 morpholine:1 DEA: 0.6 SiO₂: 0.1 MeO: 70 H₂O | Mn    |
| S-5      | Al₂O₃: 1.0 P₂O₅: 3.0 morpholine:1 DEA: 0.6 SiO₂: 0.1 MeO: 70 H₂O | Ni−Mn |
| S-6      | Al₂O₃: 1.0 P₂O₅: 2.0 morpholine: 1.0 DEA: 1.0 TEA: 0.6 SiO₂: 0.1 MeO: 70 H₂O | Ni−Mn |
2.2. Characterisation

The crystallinity and phase purity of the samples were identified using an X-ray diffractometer (Equinox 3000) operated at room temperature (\(\lambda = 1.54056 \text{ Å}\)). The Brunner–Emmett–Teller (BET) surface area of particles were measured by nitrogen gas adsorption at 77.35 K using the Autosorb-1 (Quantachrome) analyser. From isotherms, the pore volume and external surface areas of prepared samples were calculated using the t-method, and the pore size (diameter) was determined by the Saito-Foley (SF) method. The shape and particle size of catalysts were observed by using the scanning electron microscope (SEM, MIRA II-TESCAN). The particle diameters of the MeAPSO-34 samples were estimated by measuring the particle size of the particles on SEM images using Microstructure Measurement software. The chemical composition of metals in structures of calcined samples was determined by the energy-dispersive X-ray spectrometer (EDX, Philips XL30 30 kV).

The acidity of the samples was measured by ammonia temperature-programmed desorption (TPD). The amount of ammonia desorbed from the catalyst was measured.

2.3. MTO reaction

MTO performance of prepared catalysts was measured in a fixed bed reactor at the atmospheric pressure. About 0.6 g of the catalyst was inserted in the centre of the stainless steel reactor (internal diameter: 15 mm). For activation of catalyst, nitrogen flow about 100 mL min\(^{-1}\) for 1 h at 773 K was used, then the feed (CH\(_3\)OH/H\(_2\)O volume ratio of 20/80) with 0.3 mL min\(^{-1}\) was pumped into the reactor after the nitrogen flow was turned off (in atmospheric pressure and 723 K). The weight hourly space velocity was 4.7 h\(^{-1}\). The products were analysed by using Agilent 6890N gas chromatograph.

3. Results and discussion

3.1. XRD

The X-ray diffraction (XRD) patterns of prepared samples are shown in Figure 1. According to the XRD patterns, the positions of diffraction peaks of all the synthesised samples are similar to the pattern of SAPO-34 as reported.[13] On the other hand, there is no additional peak of impurity phase in all the samples. In fact, since metal concentration in various MeSAPO-34 catalysts is very low, the XRD measurements are not helpful in determining any extra-framework metals in these materials and its subsequent effects of incorporating metals in SAPO-34 are not clearly detectable with XRD.[14]

The relative crystallinity of metal-incorporated samples was calculated and reported in Table 2. Among the materials prepared by the use of two templates, the highest crystallinity was observed for Mn-containing samples, probably because the presence of different metals can affect the crystal growth in a distinct way. The substitution of transition metal ions (TMI) into the structure of the SAPO-34, because the M–O (M = Mn or Ni) bond lengths (1.9–2.0 Å) are longer than the typical T–O (T = Si, Al or P) bond of SAPO (1.5–1.7 Å), affects the crystallinity of particles.[15]

Furthermore, the lower crystallinity was observed for the NiAPSO-34 samples. The crystallinity of S-5 (which Ni and Mn are incorporated into SAPO-34 simultaneously) is higher than the crystallinity of S-1 and S-2 samples. From this result, it can be concluded...
Figure 1. XRD patterns of prepared samples: (a) Ni-incorporated samples, (b) Mn-incorporated samples, (c) Ni–Mn-incorporated samples.
that incorporation of manganese into the NiAPSO-34 framework results in increasing the crystal growth and so the higher crystallinity. By a comparison between samples S-5 and S-6, it can be found that the addition of TEA improves the crystallinity of MeAPSO-34.

3.2. EDX

The compositions of the prepared MeAPSO-34 samples measured by EDX are given in Table 3. Therefore, it is confirmed that the metal contents are successfully incorporated in SAPO-34 by the DGC method.

TMI can be incorporated by three different methods: impregnation, ion-exchange or isomorphous substitution.[16] Isomorphous substitution in dense oxides is defined as the replacement of an element in the crystalline framework by another element in the crystalline framework with similar cation radius and coordination requirements.[13] A great number of solid catalysts are produced by extending the desired metal ions through the pores or over the surface of a carrier by means of impregnation. Therefore, it is clear that more direct evidence of isomorphous substitution is needed. Several spectroscopic techniques have been used to distinguish between framework and extra framework TMI.[16]

Xu et al. [17] reported that in the case of SAPO-34, the ratio of \( \frac{\text{Si} + \text{P}}{\text{Al}} \) should be equal to 1 and the formation of the MeAPSO molecular sieve could occur as the silicon and metal are replaced with Al and P island.

In addition, if the ratio of \( \frac{\text{Si} + \text{P}}{\text{Al} + \text{Me}} \) were equal to or more than 1, the incorporation should be taken as a partial replacement of Al by Me ions and if the ratio of \( \frac{\text{Si} + \text{P}}{\text{Al} + \text{Me}} \) was less than 1, metal ions could be incorporated into the framework by replacing silicon. In Table 3, for all the samples except Mn-incorporated samples, the \( \frac{\text{Si} + \text{P}}{\text{Al} + \text{Me}} \) ratios were less than 1, indicating that silicon was partially replaced by Me ions. According to S-3 and S-4, the ratios of \( \frac{\text{Si} + \text{P}}{\text{Al} + \text{Me}} \) were more than 1 and demonstrated some of the Al replacement by Me ions. The higher Si and lower Al concentration of these samples than other samples demonstrate this result. This could be an evidence for the incorporation of metal ions into the framework.[17]

As expected, the metal content of the S-2 and S-4 samples is greater than S-1 and S-3, respectively. They exhibited high crystallinity and have the largest particles. Also, between S-5 and S-6 samples, it is found that by the addition of one other template such as TEA

| Samples | Product composition (wt%) | Mn content (wt%) | Ni content (wt%) |
|---------|---------------------------|-----------------|-----------------|
|         | Al | P | Si | Gel | Product | Gel | Product | "A |
| S-1     | S-1 | 38.26 | 11.38 | —   | —     | 0.66 | 0.94     | 0.98 |
| S-2     | 49.2 | 38.93 | 9.88 | —   | —     | 1.29 | 1.99     | 0.95 |
| S-3     | 47.27 | 40.01 | 11.98 | 0.48 | 0.74  | —   | —       | 1.08 |
| S-4     | 46.5 | 40.64 | 11.68 | 0.98 | 1.51  | —   | —       | 1.08 |
| S-5     | 50.21 | 35.67 | 11.48 | 0.44 | 1.02  | 0.66 | 1.62     | 0.90 |
| S-6     | 50.07 | 38   | 10.82 | 0.45 | 0.61  | 0.67 | 0.5     | 0.95 |
Figure 2. SEM images of prepared samples.
into the initial gel, this substitute is decreased and the metal content of S-6 is lower than
the S-5 sample.

3.3. SEM

SEM photographs of MeAPSO-34 particles are presented in Figure 2. As shown in the
figure, all the samples have uniform cubic particles with chabazite-like structure, but are
different in particle size. According to the SEM images, it was found that the samples with
high metal content have greater particles with high crystallinity (S-4 and S-6) and which
is confirmed by Zhang et al. [18]. Since the five samples (S-1, S-2, …, S-5) have identical
templates, this result shows that the nucleation for all the catalysts are different according
to metal species incorporated without consistency and nucleation effects during the
hydrothermal treatment step is probably affecting the crystal size.[5,6] Moreover, the
result shows that the ranges of particle size of S-5 and S-6 samples are lower than other
samples and the size distribution is narrow, so that the largest particles of these samples
are about 800 nm.

The results of the prepared samples demonstrate the advantage of the DGC method.
According to other investigations, the sizes of the particles of MeAPSO-34 produced in
this paper are much smaller than the particles of MeAPSO-34, which are synthesised by
other methods.[19] Since in the DGC method, most of the water has been removed, due
to lack of bulk liquid, the mass transportation is limited, which may slow down the parti-
cle growth rate and result in a smaller size of the final particles.[20] Furthermore, the
research works demonstrate that the mixed template method is an effective way to modify
SAPO-34 morphology. The composition of templates that used in the synthesis of SAPO-
34 is affected on relative crystallinity, crystal size and surface area, and mixing various
templates results in a pure SAPO-34 structure formation as well as in the size distribution.
For comparison morphologies between S-5 and S-6, the templates are important. Com-
bining TEA with other templates has no effect on the crystal size but increases the crystal-
linity.[12]

3.4. BET

The BET results of S-1, S-4 and S-6 samples (S-1 and S-6 have similar Ni content; S-4 has
the same metal content of S-6) are shown in Table 4. From the table, it can be summarised
that the surface areas vary with the crystallinity of the synthesised MeAPSO-34s. The
results show that the Mn-incorporated sample has the highest BET surface. The BET sur-
face area of the S-4 and S-6 are the same and higher than S-1. This result may be due to
their high crystallinity.[12] The NiAPSO-34 sample (S-1) has the least BET of about
368 m² g⁻¹. It can be said that the sample which has low crystallinity has a lower surface

| Sample | BET area (m² g⁻¹) | External Micropore volume (cm³ g⁻¹) | Pore diameter (nm) |
|--------|-----------------|----------------------------------|-------------------|
| S-1    | 368             | 36.5                             | 0.16              | 3.27              |
| S-4    | 527             | 42.9                             | 0.26              | 3.48              |
| S-6    | 523             | 42.1                             | 0.24              | 3.31              |
area. For the reason that, increasing the crystallinity results in the formation of more structural pores and it may enhance diffusion rate and quantity into structure channels in the crystallites, so makes the higher BET surface area in the samples.[2,21] Also, the presence of metal in the structure has its effect on the BET results, but their influence is not completely clear. This result can be determined by comparing the SAPO-34 samples which are prepared by the DGC method and without metals.[22] Pore diameters of S-1 and S-6 samples are similar to each other, but these values are less than the pore diameter of S-4.

3.5. MTO reaction

The catalytic performances of the three samples (S-1, S-4 and S-6) are evaluated. As indicated in Figure 3, all MeAPSO-34 catalysts are not activated in the first minutes of the process. A similar behaviour can be observed in some other works.[23,24] The induction period in the early time on stream is causing to incomplete conversion of methanol, which can be explained by the hydrocarbon pool (HP) mechanism. Also, due to the small cage size of the MeAPSO-34 molecular sieve, the hydrocarbon materials formed in the cages, and they work as a diffusion barrier for methanol and lower olefins. Therefore, methanol conversion is improved by increasing the concentrations of hydrocarbon materials, because they act as an active intermediate to produce lower Olefins from methanol.[25] This is a common particularity of the MTO reaction related to the build-up of the HP, which is required for catalytic activity.[26]

According to Figure 4, selectivity to short-chain olefins (C2 = C3 = ) reached a nearly constant level close to 90% (particularly in the case of S-6). This results in an increasing total selectivity for the light olefins over a certain period of time. Figure 4 also shows that the total selectivity for the light olefins increases with time on stream, especially, in the cases that have been produced using dry gel without the metal.[22]

As shown in Figure 5, the ethylene selectivities of S-1 and S-4 samples were rising, but the propylene selectivities increase for a short time and then decrease. This may be ascribed to the changes in pore size caused by coke deposition.[27] The coke deposition reduced the pore size of samples, and the selectivity of propylene with larger molecule size is decreased. The ethylene molecules are smaller than propylene, thus the selectivity to propylene increases at the beginning and decreases with further reduction in pore size.

Figure 3. Methanol conversion over the prepared samples.
Figure 4. Selectivity of light olefin over the prepared samples.

Figure 5. Selectivity of (a) ethylene and (b) propylene over the prepared samples.
Also, with an increase of propylene production at higher reaction temperature (>400 °C), propylene might oligomerise to bigger oligomers, which can consequently be cracked to form ethylene.[28]

However, in the case of S-6 catalyst, the selectivity for the smaller ethylene molecules increases for 80 min, and similar to propylene selectivity, it remains constant with time on stream. This is because it has a higher crystallinity and smaller pore size than other samples. Also, the increasing yield of ethylene by the decreasing of propylene yield is a sign of decreasing free volume in the pore structure of catalysts due to the pore size of this sample being smaller than S-4. These large multi-ring species, acting as organic centres for methanol conversion in the inorganic structure of MeAPSO-34, could adsorb fewer methyl groups due to the pronounced steric hindrance imposed by the pore structure of S-6 samples and are more prone to produce ethylene instead of propylene.

Increasing the crystallinity results in the formation of more structural pores and may enhance the diffusion rate and quantity of reactants into structure channels in crystallites. On the other hand, the MeAPSO-34 catalyst with higher crystallinity enhances the availability of methanol into its cages, resulting in better catalytic performance and increase in ethylene production.[22]

The weak and strong acidities of the MeAPSO-34 catalysts were calculated and shown in Table 5, although the acid sites are distinct for samples of different metal contents. As a result of the addition of metal ions in the structure, it introduced both ion exchange capacity and catalytic acid activity.[5] The S-4 sample has a slightly higher acid site concentration than S-6, which could be active for MTO conversion. The corresponding acid sites cannot convert methanol at the reaction temperature in early time. A variation of the amount of TOH weak acid sites has no effect on the MTO performance of MeAPSO-34 samples.

Mutation of the amount of weak acid sites has no effect on the MTO performance of MeAPSO-34 samples.[6] The concentration of bridging hydroxyl groups, which should be active in MTO conversion, varies with the Si and metal content and also the metal type of samples.

According to TPD results, the concentration of acid sites varies with the type of metals in the framework. This is ascribed to the decrease in the number of acid sites in S-6 sample compared with S-4 catalyst by incorporation of only Ni in the structure of MeAPSO-34. In fact, the acid site as well as the strength was important and all the acid sites have been considered in ethylene synthesis from methanol. This result is related to the little acid site in catalysts, which enhanced the ethylene selectivity on methanol conversion.[6]

Among the light olefin products, Mn and Ni incorporation is helpful for propylene generation, but samples with a mixture of Ni and Mn favour the ethylene production. These observations mentioned above predict the properties and catalysis difference of MeAPSO from each other, while the correlation between metal’s substitutions into the SAPO framework with catalytic property improvement is still not very conclusive.[28]

Table 5. TPD analysis of the prepared samples.

| Samples | Low temperature (°C) | High temperature (°C) | NH₃ desorbed in low temperature (mmol g⁻¹) | NH₃ desorbed in high temperature (mmol g⁻¹) |
|---------|----------------------|-----------------------|------------------------------------------|------------------------------------------|
| S-4     | 235                  | 451                   | 1.74                                     | 3.44                                     |
| S-6     | 245                  | 488                   | 0.78                                     | 2.33                                     |
4. Conclusion

In this paper, the effect of the incorporation metals (Ni, Mn and a mixture of Ni and Mn) into the SAPO-34 structure was analysed using the DGC method. For the synthesis of these samples, two or three templates were applied. The results of the prepared samples demonstrate the advantage of the DGC method, according to the SEM figures and other investigations. The particles of MeAPSO-34 produced by this method are much smaller than the particles of MeAPSO-34, which are synthesised by other methods. By energy dispersive analysis of X-rays (EDAX) analysis, it can indicate that the metal ions are incorporated into the framework of SAPO-34. According to the TPD results, the concentration of acid sites varies with the type of metals in the framework. The performances on methanol conversion for these catalysts were different according to the properties of metals incorporated into the SAPO-34 structure. The catalytic performance demonstrated high activity and light olefins selectivity for the prepared catalysts. Among the light olefin products, Mn and Ni incorporation is helpful for propylene generation, but samples with Ni and Mn favour the ethylene production.

Disclosure statement

No potential conflict of interest was reported by the authors.

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