

Synthesis of a Zeolite Y Coating on Stainless Steel Support

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The coating of stainless steel with zeolite Y was achieved. Zeolite Y crystals were shown to grow directly on the support provided the synthesis mixture was previously seeded. A stable, supported crystalline monolayer can then be synthesized with crystals as small as 0.2 μm . Using an unseeded synthesis mixture results in poor coverage and very low stability of the Y coating or in a stable coating of a side species, namely gmelinite. The stability of the zeolite Y coating on stainless steel is explained by the crystal growth in the nearest vicinity of the support. Partly uncompleted crystals are synthesized in this process and stabilized through chemical bonding with the support. The bonding with the support and thus the coverage are improved by an oxidic layer on the surface which can be formed upon calcination at high temperature.

Introduction

Catalytic distillation is a process with potential for many organic conversions.¹ Current processes using heterogeneous catalysts suffer from the fact that the catalyst is packed in "tea-bag" structures, i.e., is actually in fixed-bed conditions which induce pressure drop. Fixed-bed drawbacks would be avoided by using solid catalysts directly supported on structured packings. The coating of metallic supports is thus of great interest. Due to the number of reactions they can catalyze,² zeolites are potential catalysts to be used in these processes and the use of zeolitic coatings for different reactions has already been reported,³ mainly for silicalite-1 and ZSM-5 coatings.^{4,5}

Zeolitic coatings have already been reported on several supports.^{6,7} The literature on thin-film formation and membrane synthesis brings some data on the way supported zeolites can be made. The synthesis is generally performed via a classical hydrothermal treatment. MFI-type membranes have been prepared in this way on stainless steel⁸ and on an alumina support.^{9,10} On the latter kind of support, Kusakabe et al.¹¹ claimed to have formed a zeolite Y membrane. The synthesis

required the use of seeds in the form of small particles of zeolite X without which no film formation was possible. Thin films of zeolite A and L were achieved using a colloidal seed solution. Seeds were deposited on the support after evaporation, and film formation occurred after a secondary growth process.^{12,13} A new method was developed recently to achieve the deposition of very thin films of zeolite,^{14,15} which also involves the use of seeds. To induce the adsorption of the seeds on alumina or silica supports, the treatment of the support in a polymer is required to reverse the residual charge of the surface. Alternative synthesis is possible in the gas-phase by the so-called "vapor-phase transport" method. With this method composite membranes of various zeolites (analcime, mordenite, ferrierite, and ZSM-5) on an alumina support were prepared.¹⁶

Zeolite deposition on oxidic supports has been investigated to some extent; however, data on the use of metallic supports are not so numerous^{3,4,8,17} and concern almost only ZSM-5. A membrane of the zeolite UTD-1, a 14-member ring, has been prepared recently on silicon and porous stainless steel supports by pulsed laser ablation.¹⁸ Yet coatings of large pores zeolites have hardly been investigated whatever the support. Zeolite Y film formation was reported on copper plates.¹⁹ A stable film, ranging from 1 μm to 1 mm in thickness, was obtained with a crystal diameter of 3 μm . Valtchev and Mintova²⁰ performed the synthesis of Y films on

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various metallic supports. However except for a very specific material (97% Fe), they were not able to obtain a coating on stainless steel. Furthermore the film formed on this steel with high iron content showed low adhesivity and thermal stability.²¹ Nevertheless due to its mechanical and thermal properties stainless steel, and especially stainless steel with high chromium and nickel content, would be an appropriate support for catalytic distillation purposes, this material being inexpensive and easy to handle. Here we report the synthesis of a zeolite NaY coating on unmodified stainless steel. This was achieved by comparing different types of synthesis mixtures obtained with or without seeding. The influence of the synthesis parameters will be discussed and an explanation of the crystal growth on the steel support will then be proposed.

Experimental Section

Zeolite synthesis mixtures were prepared from two different mixture types, both of general molar composition: $10 \text{ SiO}_2 \cdot 1 \text{ Al}_2\text{O}_3 \cdot x \text{ Na}_2\text{O} \cdot 180 \text{ H}_2\text{O}$. For both mixtures sodium aluminate (Riedel de Haen: 54% Al_2O_3 , 41% Na_2O), sodium hydroxide and demineralized water were used.

Synthesis mixtures of type **S1** were made with colloidal silica (Ludox HS-40 (Du Pont)) with $x = 3, 4, 4.6, \text{ or } 10$. Different Na_2O ratios were generally obtained by keeping the amounts of sodium aluminate constant while increasing the amounts of NaOH added. In a second set of experiments, to check the influence of the pH, the sodium concentration was increased by adding various sodium salts. Starting from a mixture where $x = 3$, $\text{OH}^-/\text{SiO}_2 = 0.35$, sodium salts (NaBr , Na_2SO_4 , Na_3PO_4 , NaNO_3 , or NaCl) were added to obtain $x = 3.5, 4, \text{ and } 4.6$.

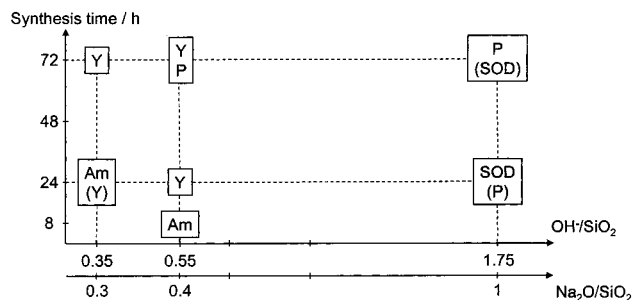
For synthesis mixture type **S2**, we used sodium silicate (Aldrich). A first mixture (seeding mixture) was prepared with $x = 10.7$, $\text{OH}^-/\text{SiO}_2 = 1.75$. It was stirred for various times (1–48 h) and further aged at room temperature for 24 h. Subsequently part of this mixture was added to the feedstock gel ($x = 5.2$, $\text{OH}^-/\text{SiO}_2 = 0.8$) leading to a mixture of final composition $x = 5.6$.

A nonporous stainless steel of quality 316L (65% Fe, 18% Cr, 12% Ni, 2% Mo, <0.03% C) was used as a support. It was shaped as plates $1 \text{ cm} \times 1 \text{ cm} \times 5.1 \times 10^{-3} \text{ cm}$. Prior to use plates were etched according to Davis' procedure¹⁹ in KOH (2.2 M) and HCl (37%) before rinsing with water and drying at 393 K. In some other experiments the steel surface was deliberately oxidized by a treatment in air at 813 or 923 K for 10 h.

Static or rotational conditions were applied for the synthesis and a 50-mL autoclave with a Teflon lining was used. Under static conditions the support was positioned horizontally on the bottom of the autoclave or was occasionally inserted in a vertical position on a Teflon holder in the middle of the autoclave. In another set of experiments the autoclave was rotated at 60 or 180 rpm, the support being inserted on the same Teflon holder connected to the lid. In all cases synthesis was performed at 373 K. After a few hours synthesis and subsequent cooling, loose zeolite powder was always obtained in the autoclave in addition to the support. The powder and the support were then washed separately with demi-water and dried at 393 K.

Powders were characterized by XRD (Philips PW1840, Cu $\text{K}\alpha$ radiation) and ICP-AES. Parent metal support and zeolite-covered supports were characterized by XRD (θ - θ diffractometer AXS D5005, Cu $\text{K}\alpha$ radiation), SEM (Philips XL20; tension used for the electron beam, 15–25 kV), and EDS

Scheme 1. Crystallinity of the Powder Using Mixture S1 in Static Conditions^a



^a Abbreviations: Am, amorphous phase; SOD, sodalite; text in parentheses, small amount.

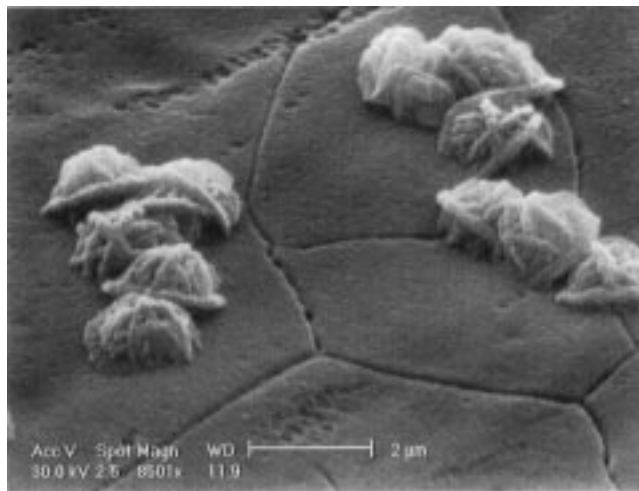


Figure 1. Isolated supported gmelinite crystals (tilt 60°).

coupled with a SEM (JEOL JSM-6400F; tension used for the electron beam, 12 kV).

Stability was checked through an ultrasound treatment in water (40 min, 50 W, 50 kHz). Thermal stability was checked by calcination at 813 K in air (10 K/min) for 5 h. The support was then quenched in water at room temperature. Finally another ultrasound treatment in water was carried out, followed by drying.

Results

I. Unseeded solution S1. Using a synthesis mixture comparable in composition, Davis et al.¹⁹ and Valtchev et al.²⁰ obtained zeolite Y coatings on copper. We made use of such a synthesis mixture (mixture type S1) with a stainless steel support. Static as well as rotational conditions were applied.

Static Synthesis. Under static conditions zeolite Y was obtained in the powder over a large range of synthesis conditions. Crystalline phases obtained at various synthesis times and concentrations and identified by XRD of the powder are summarized in Scheme 1.

At low $\text{Na}_2\text{O}/\text{SiO}_2$ ratio ($x = 3$), although XRD only evidenced the diffraction peaks of zeolite Y, SEM of the powder showed that spherulitic crystals were also present. When using the support in vertical position, only half spherulitic species were present on the support, presumably gmelinite (Figure 1). This indicates a segregation effect in this synthesis mixture induced by a lower homogeneity.

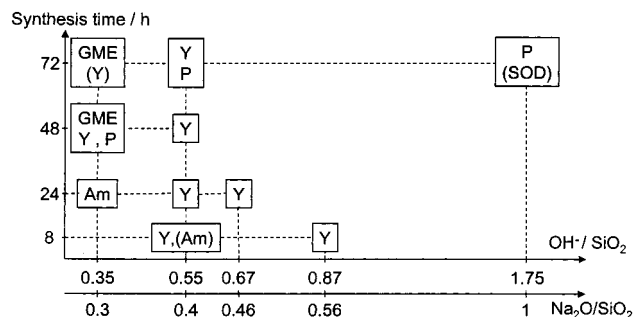
At a higher Na_2O concentration ($x = 4$) some Y crystal deposit was observed on the stainless steel support. On the metal plate set horizontally in the autoclave, the

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Scheme 2. Crystallinity of the Powder Using Mixture S1 in Rotational Conditions^a



^a Abbreviations: Am, amorphous phase; GME, gmelinite; SOD, sodalite; text in parentheses, small amount.

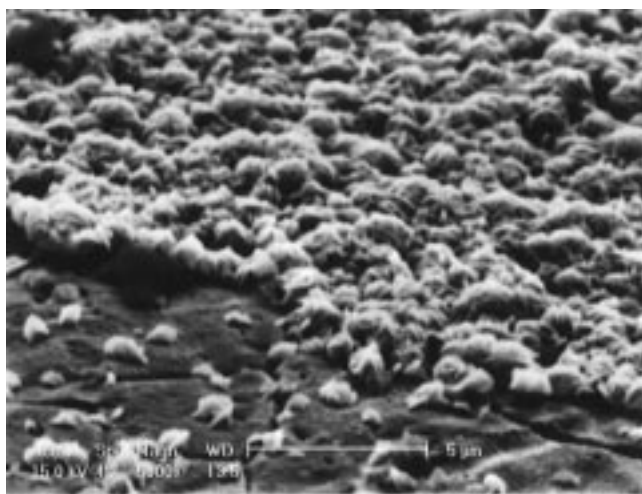


Figure 2. Support coverage with a gmelinite layer (tilt 60°).

side facing the bottom of the autoclave always remained bare as previously reported by Davis et al.¹⁹ Only on the top side were Y crystals observed. SEM characterization evidenced that these crystals were only lying on the surface. Apparently the deposit of Y observed is probably due to the mere physical bonding of the powder onto the support after gravitation or electrostatic forces led crystals to the support. To eliminate the effect of the gravity and to improve the homogeneity of the gel a rotation synthesis was applied.

Rotational Synthesis. Syntheses performed at 60 or 180 rpm did not show any differences neither in the free powder nor on the support. Therefore, 180 rpm was thus chosen to ensure the best homogeneity in the mixture. Scheme 2 reports the crystalline characteristics of the powder obtained in various synthesis conditions at 180 rpm and determined after XRD analysis. In the powder differences were observed compared to static synthesis (cf. Scheme 1). They were especially obvious for $x = 3$. After 72 h of synthesis, only a structural equivalent of gmelinite (zeolite S²²) was obtained. The crystals on the support and in the free powder showed the same diameter (2–3 μm), but on support only half-shaped crystallites were observed, indicating chemical bonding to the steel. The coverage obtained was very dense on both sides of the support, except for the area which was inserted in the Teflon holder, as can be seen in Figure 2. The layer was mainly one crystal thick. Upon ultrasound treatment this layer remained attached to the support, confirming the good binding of the crystals to

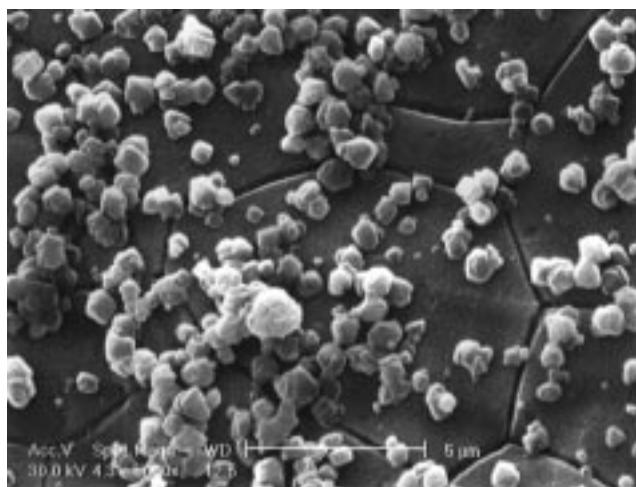


Figure 3. Zeolite Y crystals on support after synthesis S1.

the stainless steel. A supported gmelinite had already been grown on polymer substrates but its synthesis required the use of a template.²³ The method described here can then be an alternative to grow a dense gmelinite film on a support.

According to results obtained in static conditions, to synthesize NaY rather than gmelinite the sodium oxide content in the synthesis mixture should be increased. This was achieved by increasing the NaOH content. With a $\text{Na}_2\text{O}/\text{SiO}_2 = 0.4$ (pH = 12.25), the results obtained were the same as in static conditions (Scheme 2) except that in rotational conditions, Y crystallized already after 8 h. However although crystallization occurred faster, the behavior at longer synthesis times was not modified and after 72 h, zeolite P was the only side species indicating a low reactivity of the synthesis mixture.

A slightly better coverage of the support was obtained than under static conditions. On the support as well as in the free powder, crystals were about 0.8–1 μm in size. The powder showed Si/Al and Si/Na ratios of 2.5 and 2.4, respectively. However supported crystals were just weakly attached (Figure 3), upon ultrasound treatment in water the surface was swept clean and all crystals disappeared.

To check if the bad adhesivity of Y crystals was related to the high pH, we increased the Na_2O content by adding various amounts of sodium salts while keeping the pH constant (pH = 11.7). Results obtained after XRD of the powder and SEM characterization are summarized in Table 1. After 24 h of heating, the powder was not completely crystallized regardless of the concentrations of the salt added. However even after such a short time the only species obtained was gmelinite. Even when it was not evidenced by XRD of the powder it was seen with SEM on the support. Hence the Na_2O concentration does not have any influence on the ability to crystallize Y if the pH is too low which is coherent with previous results.²⁴ Besides the lower pH does not assist the binding of the zeolite on support.

In conclusion, although faujasite was synthesized in the powder using preparation S1 for various gel com-

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Table 1. Influence of the Sodium Source on the Crystallinity (Mixture S1)^a

	synthesis time, h	Na ₂ O/SiO ₂		
		0.35	0.4	0.46
NaBr	24	Am	Am	Am
Na ₂ SO ₄	24	Am	Am + GME	Am + GME
Na ₃ PO ₄	24	—	Am	—
NaNO ₃	24	—	Am+GME	—
NaCl	24	—	Am + (Y)	—
NaBr	72	—	GME + (Y)	—
Na ₂ SO ₄	72	—	GME	—

^a Abbreviations: Am, amorphous phase; GME, gmelinite; text in parentheses, small amount.

Table 2. Crystallinity of the Powder after Synthesis with Mixture S2^a

	synthesis time, h					
	6	7	8	18	24	72
phase obtained	Am + Y	Y	Y	Y + (GIS)	GIS + (Y)	GIS

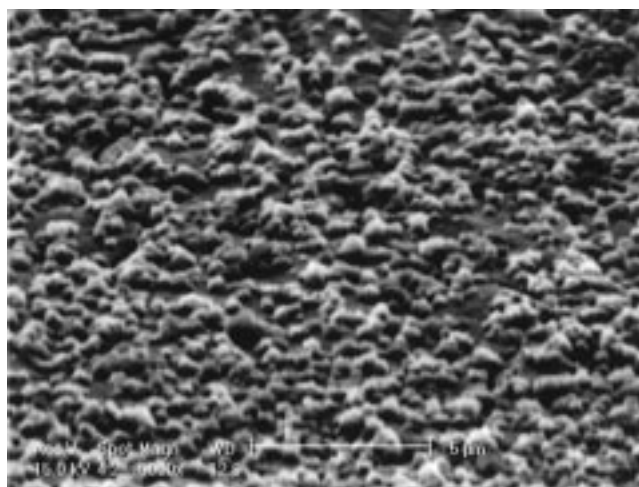
^a Abbreviations: Am, amorphous phase; GIS, gismondine (~gobbsinite); text in parentheses, small amount.

positions and synthesis times, we did not succeed to bind zeolite NaY onto stainless steel 316L. However while working at lower pH, we showed that binding a zeolite (gmelinite) on stainless steel was possible. Hence the problems encountered to crystallize zeolite Y on this specific support are likely to be due to the synthesis mixture itself or to the interactions between the gel and the support. The relatively large size of the crystals evidences a low concentration of nucleating particles.²⁵ Concentrations of nucleating particles close to the support are thus quite low and crystal growth on support cannot occur to a large extent. Therefore to increase the number of nuclei on the steel we made use of a seeded mixture.

II. Seeded Solution S2. Seeds were synthesized^{24,26} by aging at room temperature a synthesis mixture highly concentrated in Na₂O (see Experimental Section) and were added to a solution containing lower amounts of Na₂O. This seeded mixture coded S2 showed a different behavior than S1. The crystalline phases obtained after various synthesis times in the powder are summarized in Table 2.

Unlike mixture S1, mixture S2 shows a very high reactivity. With the latter mixture Y is formed but only within a limited range of time. Already after 7–8 h synthesis Y is the only species detected, but already after 18 h, another species is formed. This species' XRD spectrum matches that of gobbsinite. It differs from the zeolite P obtained with mixture S1. Although they have nearly the same unit cell parameters gobbsinite has a rhombohedral unit cell, whereas P has a cubic structure. This might be due to the differences in the silica sources. At longer synthesis times, gobbsinite is the only species detected.

Under the conditions where Y is made, the presence of seeds in the mixture has several consequences on both the powder and the support coverage. In the powder the Si/Al ratio (1.8) was lower than the one obtained with mixture S1. This is in agreement with previous re-

**Figure 4.** Supported zeolite Y crystals after synthesis S2 (tilt 60°).

sults^{27,28} and is due to the higher alkalinity of the seeded mixture (initial pH = 13.5). These crystals also differ from the ones made with mixture S1 by their size which was shown by SEM to be comprised between 0.1 and 0.5 μm, depending on the seeding procedure. The smaller crystal size confirms the presence of larger concentrations of nucleating particles.

These differences are reflected on the support where the seeding procedure has an important effect not only on the crystal size but also on the coverage. Using the seeded mixture after 7.5-h synthesis, zeolite Y was the only species found on the support. A large coverage was obtained (Figure 4) which, by modifying the experimental conditions can be as extended as a crystalline monolayer. An increase of the stirring time (from 1 h to 48 h) of the seeding mixture prior to addition to the feedstock gel induces a decrease of the crystal size (from 0.5 μm to 0.15 μm). For a defined stirring time, the increase of the amount of seed gel added also results in a slight decrease of the crystal size but mainly in a better coverage of the support which shows that the amount of supported crystals is directly related to the initial seed content. The combination of both effects allowed us to obtain a good coating with very small crystals (200–250 nm). When this was combined with a pretreatment of the support, namely a calcination at high temperature (813 K) prior to synthesis, it resulted in a coverage close to the monolayer. This can be seen in Figure 5 on which some spots of stainless steel can also be seen below the crystals. When a support precalcined at 923 K was used, the coverage was total. Several zeolite layers were then achieved.

XRD confirmed that Y was the only species on the support. Beside the peak originated by the metal (43.7°), a peak at 6.2° is observed, indicating that the crystals seem to be preferentially oriented on the (111) plane (Figure 6A). The XRD pattern of the supported zeolite on the support precalcined at 923 K (Figure 6B) evidences the same large peak at 6.2°. The other peaks

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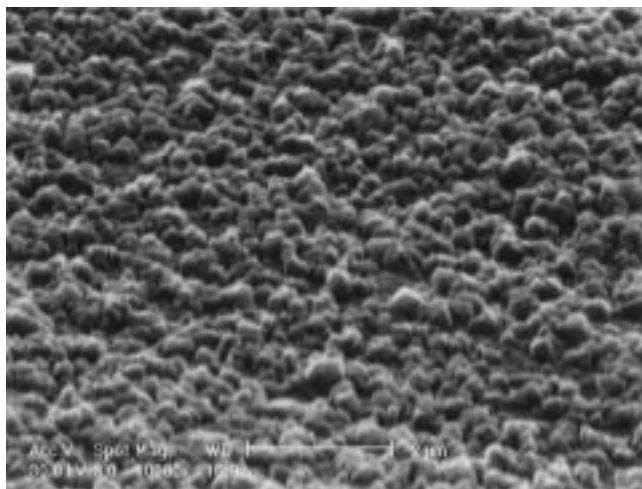


Figure 5. Supported layer of zeolite Y crystals after synthesis S2 on a support precalcined at 813 K (tilt 60°).

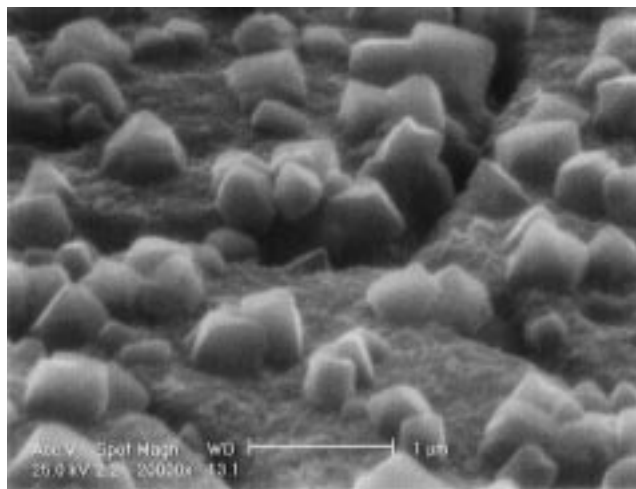


Figure 7. Isolated supported zeolite Y crystals (tilt 60°).

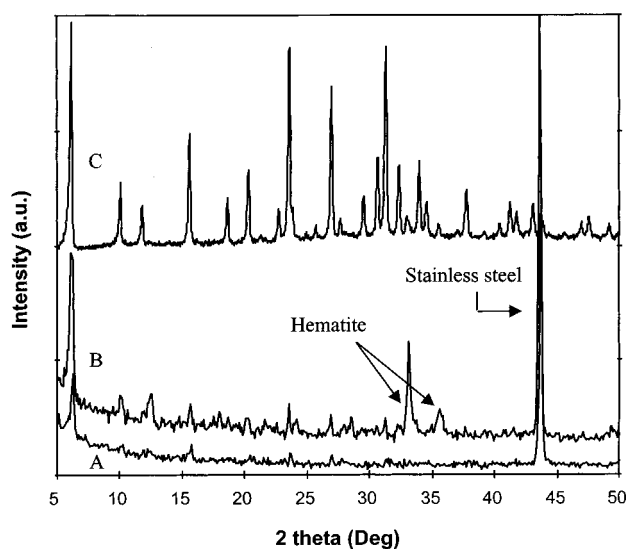


Figure 6. XRD patterns of zeolite Y supported on stainless steel (A), zeolite Y supported on stainless steel precalcined at 923 K (B) and zeolite Y powder (C).

characteristic of zeolite Y can also be seen although their relative intensity is much lower than in the powder (Figure 6C). This confirms that more than one layer was deposited. The crystals in the upper layers do not show the same preferential orientation as the ones in the first layer and are more likely to be adsorbed randomly as they grow further away from the support. In addition to the zeolite peaks and the steel peak, new peaks are observed at 33.1° and 35.6°. They are characteristic of hematite (Fe_2O_3). These peaks were also present after calcination at 813 K, but their intensity was lower. The calcination of the support at high temperature in air thus creates an oxidic layer on the surface.

Although the supported crystals show the same characteristics as the powder, it is obvious that unlike the crystals obtained with mixture S1, they are not loose crystals physically bound to the support. Figures 4 and 5 show that crystals seem to be grown "from the support". This is shown even more clearly in Figure 7 where the crystals were synthesized on purpose with a larger size by applying a lower stirring time of the seeding mixture. The crystal shape is still octahedral, as is to be expected for zeolite Y, but the crystals are

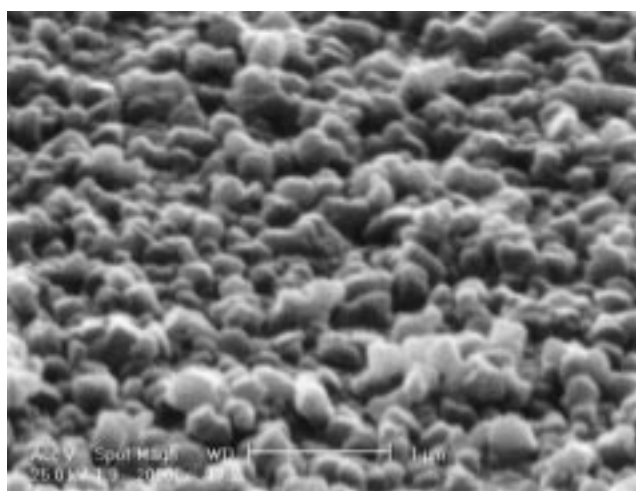


Figure 8. Supported layer of zeolite Y crystals on a precalcined support after synthesis S2, calcination at 813 K and quenching (tilt 60°).

only partly completed as their growth was stopped in the direction of the support. Crystal growth then occurred in the proximity of the support leading to quite stable crystals. Unlike crystals obtained with mixture S1 they withstand a sonification treatment. Moreover upon thermal treatment at 813 K (1 K/min) the composite system was not modified. To check its thermal stability in more drastic conditions a quick heating to 813 K (10 K/min) was applied and after 5 h at high temperature the system was quenched in water at room temperature. It was then submitted again to sonification. Although the steel is submitted to high constraints during this treatment the coverage was hardly affected (See Figure 8 in comparison with Figure 5). During synthesis a stable equilibrium state was thus reached between the support and the crystals. Therefore a stable zeolite Y coating can be achieved on stainless steel.

III. EDS Characterization. The EDS spectrum of stainless steel 316L (Figure 9A) evidences the following surface composition, which is close to the bulk composition: 65% Fe, 20% Cr, 12% Ni, 2% Mo.²⁹ No differences in composition were observed on the center of the plates or on the edges. Furthermore although the grain bound-

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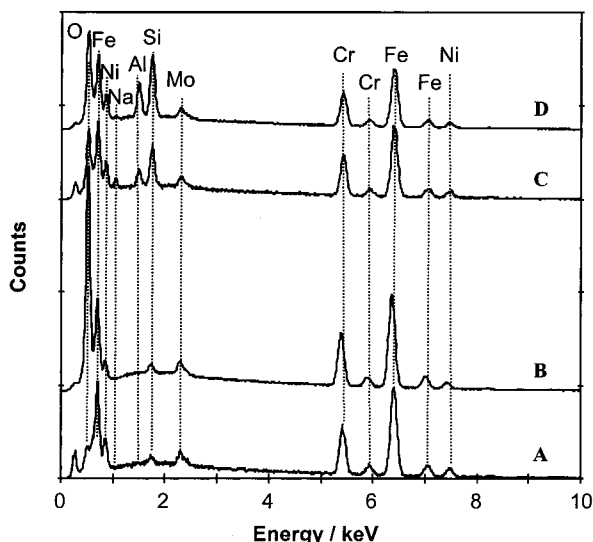


Figure 9. EDS spectra of the supports and the supported materials: (A) stainless steel; (B) stainless steel calcined at 923 K; (C) supported gel layer, synthesis mixture S1; 2 h; and (D) supported NaY, synthesis mixture S2; 8 h.

aries are clearly seen on this material after etching, no differences are observed in composition between the grain boundaries and the center of the grains.

After calcination at 923 K, EDS showed slight modifications in the steel surface composition 67% Fe, 21% Cr, 9% Ni, 2% Mo (Figure 9B). Meanwhile the ratio Fe/O was multiplied by 8. Therefore the calcination of the steel at high temperatures induces the formation of an oxidic layer on surface, mainly made of iron oxide.

A synthesis experiment S1 was stopped after 2 h of heating, hence before crystallization. Although the support was carefully washed, the EDS spectrum shows that Na, Si, and Al are present on the support (Figure 9C). The Si/Al ratio is comparable to the one of the initial synthesis mixture (~ 4). A gel layer is thus deposited on support. Peaks of iron, chromium, and nickel are still present in the spectrum, so this gel layer must be rather thin.

When stopping a synthesis experiment S2 after 2 h of heating, particles were already observed on the support, showing that crystallization had started. These crystallites have an average Si/Al ratio of 3.5, i.e., higher than the one observed in the crystallized powder. Between the particles, silicon and aluminum were also found. Hence in this case also a gel layer is deposited on the support in the initial stage of the reaction.

After complete crystallization (8 h), the supported crystals show a Si/Al ratio of 2.2–2.6 (Figure 9D). This is somewhat higher than what was observed in the loose powder (1.8). In all the supported samples the aluminum content was slightly lower than in the powder, but the sodium content was much lower than expected, sometimes even absent. The stabilization mechanism of the crystals is therefore different compared to that of the powder.

Discussion

EDS (Figure 9) showed that in the first stage of the synthesis reaction (that is before crystallization occurs), a layer containing Si, Al, and Na is deposited on support. This layer shows approximately the same Si/Al ratio as

the initial synthesis mixture. Part of the synthesis gel is thus adsorbed on the support after a short time. In the spectrum, peaks generated by the metals of the support, i.e., iron, chromium, nickel, can be observed. Given the energy used for the electron beam, the metal would not contribute to the overall signal if the covering layer was thicker than 1.5–3 μm . Hence the layer deposited is rather thin.

The unseeded synthesis mixture S1 shows a very low reactivity which is due to the low concentration of nucleating particles in the initial stage of the reaction. This is confirmed by the relatively large size of the crystals. The concentration of these nuclei in the layer deposited on support can then be assumed to be equally low and thus few crystals will grow directly on the support. Moreover crystals stabilized in the bulk of the synthesis mixture are not likely to bind to the support except through weak physical bonds. Mintova et al.^{20,21} succeeded in synthesizing a zeolite Y film on copper and on an iron-rich steel (96–98% Fe) with use of an unseeded solution. However when using a steel comparable in composition to the one we use, only isolated crystals were obtained.²⁰ On both of these steels, the concentration of nucleating particles on the support was lower than on copper as evidenced by the small amount of supported crystals²⁰ or by their large size.²¹ The authors attribute the difference between copper and steel to a partial dissolution of the copper in the alkaline synthesis mixture²¹ which creates favorable sites for crystallization and enables stronger interactions between the gel and the support. This implies that while working with a more stable support like stainless steel, especially a steel containing a high chromium concentration, which is more resistant to corrosion, interactions between the gel and the support will be weaker and the development of a zeolitic coating will be hampered. Besides if new nucleation particles are formed in the course of the synthesis, due to weaker interactions they will grow somewhat further away from the support than on copper substrates which induces a lower stability of the zeolite coating notably upon thermal treatment.²¹

By contrast, when using seeded mixtures S2, nucleation particles are present to a large extent in the initial synthesis mixture. Consequently the gel layer retained on the support in the initial stage of the reaction already contains a large number of seeds. Upon heating, seeds will first make use of the nutrients contained in the gel layer to grow. Due to the small thickness of this layer, particles are forced to grow in the vicinity of the support. In the direction of the support, growth is stopped by the metal surface leading to a crystallite whose shape is uncompleted. In the opposite direction crystallization can proceed undisturbed by making use of the nutrients of the free mixture after the depletion of the initial gel layer. The crystal morphology observed reflects these phenomena. Hence the initial gel layer is a determining factor for the coverage of the support. To obtain the highest coating of the support with crystals, it is of importance that the gel layer is well spread over the surface. This can be achieved through rotation of the autoclave which also allows coverage on both sides of the support to be obtained, and not only on the top side as reported for static conditions. This also means that gravitation does not play a role in our case.

Our results indicate that seeding is required to achieve a stable and extensive bonding on this stainless steel support. Zeolite seeds were previously used by Hedlund et al.^{14,15} to achieve the synthesis of thin films of zeolite A or silicalite-1. However, their method requires first the treatment of the support (alumina or silicon crystals) in a polymeric solution to reverse its electrostatic charge in order to allow the adsorption of the seeds prior to synthesis. Another method³⁰ involves a first step of silanation of the support prior to seeds adsorption. Once the seeds are deposited on the support they are allowed to grow in a zeolite synthesis mixture. We showed that seeding can be effective to achieve the coating of the support without these intermediate steps even on a rather inert support like stainless steel. The coverage of the support with zeolite Y will strongly depend on the seed concentration in the starting synthesis mixture. Hence by influencing the deposition of the initial gel layer and by making use of a solution containing large amounts of nucleating particles, a continuous layer of zeolite can be obtained. The presence of seeds is all the more required when synthesizing metastable zeolites such as Y. A stable layer of gmelinite was achieved on stainless steel without seeding but the longer synthesis time and the better stability of gmelinite can induce the formation of nucleating particles in the gel layer first deposited on the support. This differentiates it from the zeolite Y synthesis.

After the crystallization process, fully octahedral crystals were not observed on the support as one would expect for zeolite Y, but only partly shaped crystals derived from an octahedral shape. Once synthesized, these crystals appear to be firmly attached to the support. This is shown by the stability of the layer upon ultrasound treatment, calcination at high temperature and quenching (Figure 8). Zeolite Y is known to crystallize in the sodium form. Even when achieving the synthesis via a template route, thus yielding to the hexagonal form, sodium content is always approximately equal to the aluminum content.³¹ However in our case it is striking to see that hardly any sodium is observed in the supported crystals. After 2 h of synthesis, the silicon-to-sodium ratio was found approximately equal to 20. This ratio increases with the synthesis time and on a crystallized sample, the Si/Na ratio is on average greater than 100. The increase of the Si/Na ratio during the crystallization process indicates that as the crystal grows sodium is no longer required for building or stabilizing the structure. This implies that other elements contribute to the stabilization, probably some cations dissolved from the steel surface. This phenomenon needs further study. The presence of some amorphous phase on the surface might also account for these ratios, higher than expected.

To bind the crystals on the support, hydroxyl groups present in an oxidic layer on the surface probably play a role. Involvement of an oxide layer on the support surface in binding the crystals is consistent with the fact that zeolite Y was more easily obtained on copper

plates.¹⁹⁻²¹ Copper is more likely to be covered by an oxide layer than stainless steel. An oxide layer can be obtained on stainless steel upon calcination at high temperature. XRD and EDS evidenced the formation of iron oxide (hematite) after calcination of the steel at temperatures higher than 813 K. On a precalcined support the coverage obtained with zeolite Y was much better. Therefore the binding of the crystals on the support is largely improved when it occurs through an oxidic interface. This layer probably also favors the adsorption of the nucleating particles in the closest vicinity of the support. Nucleation and crystal growth are also possible in the physical defects created on the stainless steel after etching, and at the grain boundaries of the support. However even on the grain boundaries, the concentration of crystals does not appear larger than on the rest of the surface. Although they are probably involved in the retention of nucleating particles, the physical defects on surface are not the determining factor in the binding of the zeolite crystals. This emphasizes the role of chemical interactions on the support surface; a precalcination of stainless steel is recommended.

Conclusions

It was shown that zeolite Y can be grown on stainless steel in optimized conditions. The use of unseeded reaction mixtures is not sufficient to induce a thick coating and a stable binding between the Y crystals and the support, especially when using steels with high chromium contents. However this method can be used to achieve a supported gmelinite layer. The appropriate synthesis for Y requires the seeding of the synthesis mixture. During the first stage of the synthesis a gel layer is deposited on the support surface. The nucleating particles contained in this gel layer are thus forced to grow close to the support which leads to crystals whose growth was stopped in the direction of the support. They were shown to be firmly bound to the support surface. Chemical interactions with an oxide layer on the surface are thought to occur and to play a role in stabilizing the crystals. Such an oxide layer can be established by precalcination of the support. Complete coating of the stainless steel is then achieved.

A stable zeolite Y monolayer has thus been synthesized. The use of these supported zeolitic crystals in catalysis can now be considered which implies that the specific activation of this material has to be studied. To achieve a good catalyst possibilities to ion exchange or dealuminate the supported Y are investigated now. It should be noted that besides applications in catalysis the use of zeolitic coatings for other purposes such as sensor devices could be envisaged. NaX for instance was shown to be a sensitive material for hydrocarbon detection.³² As-synthesized supported zeolites could then also find a direct application.

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