Design of Stable Palladium-Based Zeolite Catalysts for Complete Methane Oxidation by Post-Synthesis Zeolite Modification

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Abstract

Catalytic methane oxidation is used in exhaust gas aftertreatment to reduce methane emissions from lean-burn natural gas vehicles as well as in stationary combustion processes. Pd/zeolite catalysts provide high activity for this reaction, but they deactivate rapidly under reaction conditions and in the presence of steam due to extensive palladium nanoparticle sintering, which is a common deactivation pathway for supported catalysts. Understanding the origin of this phenomenon is crucial for improving the performance of such materials. In this work, we identify all stability and activity descriptors of Pd/zeolites fully exchanged with sodium. Based on these descriptors we design an active and stable catalyst using the synthetic approach which comprises formation of mesopores in the zeolite by mild desilication, removal of surface and extra-framework aluminum by selective dealumination and complete sodium post-exchange. This allows to turn unstable Pd/H-ZSM-5 into a highly active sintering-resistant hierarchical Pd/Na-ZSM-5 for the demanding reaction of complete methane oxidation. This synthetic procedure can be applied to other zeolites to enhance stability of supported catalysts that are prone to sintering.

Keywords: methane oxidation, exhaust aftertreatment, palladium, hierarchical zeolite, desilication, constrained mesopores

1. Introduction

Lean-burn natural gas engines significantly reduce carbon dioxide emissions and increase the overall fuel efficiency both in stationary and automotive applications. The advantages of natural gas as a fuel include lowest hydrogen-to-carbon ratio among all hydrocarbons, high abundance and an already existing distribution network. Moreover, methane can also be produced from biogenic sources enabling a smooth transition to a renewable energy system by substituting increasing shares of natural gas by biomethane.¹ The main concern about methane as a fuel is that state-of-the-art catalysts lack low-temperature activity and long-term stability, leading to methane emissions in the exhaust gas.²⁻⁶ Typical methane oxidation catalysts comprising a noble metal, preferably palladium highly dispersed over a support material,⁶⁻¹⁷ suffer from rapid deactivation under reaction conditions induced by the active phase sintering.¹⁸⁻²¹

Stabilization of metal nanoparticles in the constrained inner space of a support has attracted increasing attention in recent years.²²⁻²⁶ Such approach allows to physically encage metal particles, allowing the reactants to diffuse through the bottle-neck pores, which are non-permeable to the constrained metal nanoparticles due to size restrictions. This approach is especially relevant for expensive precious metal-based catalysts, allowing to drive down the materials costs by decreasing the amount of the active metal. In addition, enhanced stability prolongs the operation time, further improving the economics of the process. Numerous support materials and encapsulation methods have been reported for various metals. For instance, in the case of precious metals, Seo et al. encapsulated palladium particles in amorphous silica-alumina by coating the metal nanocrystals.²⁷ Post-synthetic zeolite recrystallization was used to produce encapsulated platinum particles in hollow zeolite nanospheres.²⁸ A similar result was achieved by alkaline post-synthesis treatment of the zeolite and subsequent impregnation of iron and platinum.²⁵ Martinez et al. used carbon nanoparticles as hard template to obtain mesoporous hollow zeolite and then deposited palladium by impregnation.²⁹ Cargnello et al. recently obtained superior methane oxidation activity over two-nanometer palladium nanoparticles coated by ceria and supported on alumina.³⁰ Palladium particles similarly coated with titania also yielded promising results.³¹ Although these approaches led to enhanced activity and stability of encapsulated metal nanoparticles, complete prevention of nanoparticle migration could not be achieved,³² thus requiring further advancements in understanding of what causes sintering and mitigation by novel synthesis strategies.

The variety of available strategies requires a rational approach to the selection of appropriate synthesis methods and materials. Metal nanoparticles should be very small, between one and two nm, to provide high surface area and reactivity^{2, 13, 30} and they should be densely packed to minimize the dimensions of the catalyst bed. A zeolite is an attractive material for encapsulation of small metal particles, as the micropores in the walls have a uniform diameter below one nanometer, which is in most cases sufficient for reactants and products to freely diffuse, but prevents the mobility of the particles of a few nanometer in diameter. The voids (mesopores) in the zeolite crystals would have an ideal size, which is comparable to the diameter of a metal nanoparticle to reach maximum loading per unit of volume. Finally, zeolites possess high integrity and stability and to large extent stand high temperatures typical for catalytic applications.³³

Mesopores can be obtained in zeolites by various methods, such as hard and soft dual templating, recrystallization, steaming, desilication, dealumination and others.³⁴⁻³⁹ Desilication by alkaline treatment yields well-defined mesopores while preserving high crystallinity and integrity of the zeolite matrix.³⁷⁻³⁸ The mesopore quality (diameter, shape and connectivity) can be controlled carefully by modifying the synthesis conditions and using additional reactants. Fodor et al.³⁷ and Milina et al.³⁸ described zeolites with constrained mesopores obtained by alkaline treatment in the presence of an organic template. While being not ideal for mass transfer limited reactions, where open mesopores are preferred, such material perfectly matches the requirements of a hierarchically structured metal-zeolite catalyst with encapsulated particles in the voids.

Dealumination with mineral acids also produces secondary pores in zeolites upon dissolution of silicon from the defect areas of the zeolite at low pH⁴⁰ and due to partial structural collapse of excessively dealuminated low silica-zeolites.⁴¹ This method, however, significantly changes the acid properties and aluminum distribution within the zeolite. Aluminum removal from the zeolite can be controlled by variation of the acid and the treatment conditions. For instance, the selective removal of aluminum from the external surface of the small-pore zeolites occurs upon the treatment with organic acids like oxalic, tartaric or acetic, since the aluminum salts of these acids are too bulky to be formed inside the micropores.⁴²⁻⁴³

There is high demand for improving the activity and especially the stability of palladium-based catalysts for the demanding reaction of complete methane oxidation and the above described strategy could be used to achieve this.

Several publications included comparison between sodium and proton forms of palladium/zeolite catalysts for complete methane oxidation. For example, Maeda et al.

compared Pd/H-MOR and Pd/Na-MOR with various Si/Al ratios and concluded that very high Si/Al ratio (260) as well as the presence of sodium cations in the zeolite negatively affected both activity and stability.⁴⁴⁻⁴⁵ On the contrary, earlier works showed that the activity of Pd/Na-zeolites can be positively correlated with the Na/Pd ratio.^{21, 44} In the above-mentioned works sodium was either initially present in the parent zeolite, or was added by ion-exchange prior to the exchange with palladium. The latter treatment produces only partly-exchanged zeolites. For example, the conventional ion-exchange procedure led to only 46% cation exchange in the case of mordenite with the Si/Al ratio of 51.⁴⁴ Recently, we showed that dealuminated Pd/H-MOR, when completely exchanged with sodium to remove all residual acid sites, yields a highly active and stable catalyst.⁴⁶ This was achieved by suppressing Ostwald ripening induced by the zeolite acidity and stabilization of palladium nanoparticles within the mesopores of the support, which were displaced from the zeolite acid sites by sodium.

In this work, we demonstrate the importance of fine-tuning the properties of zeolite supported catalysts by presenting a novel synthesis strategy, which yields methane oxidation catalysts of unprecedented activity and stability, explains the discrepancy in literature about the role of sodium cations and extends the knowledge about stability descriptors of Pd/Na-zeolites. With the goal of obtaining stable encaged palladium nanoparticles in the zeolite, we introduce a synthetic approach comprising consecutive desilication, selective dealumination, palladium exchange and removal of residual zeolite acidity by post-exchanging sodium and turn unstable Pd/H-ZSM-5 into highly active and stable mesoporous dealuminated Pd/Na-ZSM-5. We show that this synthetic procedure can be applied to other zeolite frameworks (MOR, BEA) and be used with various charge-balancing cations (Na, K and Cs) to enhance the stability of supported palladium catalysts.

2. Experimental

2.1. Catalyst synthesis

Zeolite ZSM-5 (SM-27, NH_4^+ -form, Si/Al = 13, Clariant) was calcined to produce the H-form (denoted as H-Z) and then subjected to various acid treatments (hydrochloric, nitric and oxalic acids) and base-acid treatments, which are summarized in Figure 1, with the goal to modify the aluminum distribution and the pore structure. The base treatment was carried out at 65 °C for 30 min. First, the zeolite powder (5 g) was added to the preheated magnetically stirred mixture (100 ml) containing sodium hydroxide (0.2 M) and tetrapropylammonium bromide (TPABr, 0.2 M). To control the desilication time precisely, after 30 min the slurry

was taken out of the water bath and diluted with cold deionized water (200 ml). The solid component was then separated, washed thoroughly with deionized water until the pH value was not below 8, dried at 120 °C for 24 h and calcined in a muffle oven at 600 °C for 2 h. Acid treatments were performed under a reflux at 80 °C for 4 h followed by washing with deionized water and drying as described above. After these pretreatments, the obtained materials were ion-exchanged with the required amount of $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$ solution (pH = 6) at room temperature for 24 h to obtain a nominal 1 wt% loading of palladium. After drying at 120 °C for 24 h, the final Pd/H-ZSM-5 catalysts were obtained by calcination at 500 °C for 2 h at the heating rate of 2 °C/min to ensure a high dispersion of PdO nanoparticles.⁴⁷⁻⁴⁹ Fully sodium-exchanged Pd/Na-ZSM-5 catalysts were obtained by titrating the residual acid sites of the parent Pd/H-ZSM-5 catalysts with a sodium bicarbonate solution (0.02 M) for 2 h until the pH of the slurry did not reach 7.5. The powder was then washed once with deionized water and calcined at 500 °C for 2 h. The final catalysts were denoted as Pd/A-Bc, where “A” corresponds to the form of the zeolite (H^+ or Na^+), “B” identifies whether the zeolite was desilicated (D) or not (Z), and “c” represents the type of acid(s) used in the pretreatment (c – hydrochloric, n – nitric, o – oxalic).

Mordenite zeolite (CZM-20, H^+ -form, Si/Al = 10, Clariant) was treated identically to ZSM-5, while for zeolite beta (NH_4 -BEA, NH_4^+ -form, Si/Al = 12, Clariant) the conditions of post-synthesis modifications were adjusted. Desilication was performed in a 0.1 M sodium hydroxide solution at 45 °C for 30 min, dealumination was carried out with 0.5 M oxalic acid solution at room temperature for 2 h. The thus obtained supports were consecutively loaded with palladium and sodium as described above. It should be noted that the mordenite sample received for this work was different from that used in our previous study and was not pre-treated.⁴⁶

2.2. Catalyst characterization

The palladium loading as well as the Si/Al ratio and the content of sodium in the catalysts were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian VISTA Pro AX instrument. The catalysts were completely digested in the $\text{HCl}/\text{HNO}_3/\text{HF}$ mixture (ratio 6:3:1) in a 3000 Anton Paar microwave digestion unit. The textural properties of the support were characterized by argon physisorption at 77 K using a Quantachrome Autosorb 1 instrument after degassing at 300 °C for 6 h to remove water and other adsorbed species. The support surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The pore size distribution in the range from 2 to

100 nm was calculated by fitting the argon physisorption isotherm using the density functional theory (DFT) model from the software package provided by Quantachrome. Scanning transmission electron microscopy (STEM) and secondary electron (SE) images were taken with a Hitachi HD-2700 microscope at the 200 kV acceleration voltage. Particle size distribution was obtained from counting particles in 10-15 STEM images. A Bruker D8 Advance AXS diffractometer with Cu K α radiation was used to obtain powder X-ray diffraction (XRD) patterns in the 2 θ range from 10° to 60°. Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) ^{27}Al spectra were recorded at 10 kHz (1024 accumulations) on a Bruker Avance 400 MHz spectrometer with ammonium aluminum sulfate dodecahydrate ($\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) as the reference. Transmission IR spectra FTIR measurements were carried out on a Nicolet iS50 spectrometer equipped with a DTGS detector. In a typical experiment, 20 mg of the sample was pressed into a self-supported wafer (2 cm 2). The sample was placed in a room temperature quartz glass FTIR cell with KBr windows and dried in vacuum at 400 °C for 2 h. Then, the sample was cooled to room temperature and the spectrum was recorded (128 scans at a 4 cm $^{-1}$ resolution). The background was subtracted using the OMNIC 9.1 software package.

2.3. Evaluation of catalytic activity

The activity of the powder catalysts towards methane oxidation was evaluated in a dedicated setup consisting of a quartz-glass plug flow reactor (ID = 6 mm), gas flowmeters, heating control and an outlet gas analysis system (InProcess Instruments GAM 400 mass spectrometer). Fragments with the m/z ratio of 2 (H_2), 12 (C), 15 (CH_4), 16 (O_2), 18 (H_2O), 28 (N_2), 30 (NO), 32 (O_2) and 44 (CO_2) were followed. The exothermic effect of the reaction was minimized by diluting the catalyst (50 mg, 150-200 μm sieve fraction) with cordierite (150 mg, 100-150 μm). Prior to collecting the catalytic data the catalyst was pretreated in the flow of 1 vol. % CH_4 , 4 vol. % O_2 , 95 % N_2 at 550 °C for 30 min. The reactor was then cooled to 420 °C, and 5 vol. % of steam was added to the flow to obtain the catalytic stability data in wet feed.

3. Results and discussion

3.1. Performance of the non-treated Pd/H-ZSM-5 and Pd/Na-ZSM-5

Figure 2a shows the catalytic stability tests of the variously prepared Pd/ZSM-5 catalysts. Over the non-modified Pd/H-Z, methane conversion decreased rapidly upon introduction of

steam to the CH₄/O₂ feed at 420 °C from 60% to 13% within the first three hours followed by slower deactivation. This behavior is associated with the extensive sintering of palladium and the formation of inactive Pd(OH)₂ species within the first few hours, followed by a slow degradation of the zeolite through the framework dealumination in the presence of steam.^{13, 19, 49-51} STEM images of the calcined Pd/H-Z and after reaction in the flow of 1 vol.% CH₄, 4 vol.% O₂, 5 vol.% H₂O, bal. N₂ at 420 °C for 20 h (referred to as “spent Pd/H-Z”) and the corresponding particle size distributions (Figure 3a,b) confirmed this explanation. The highly dispersed palladium particles with homogeneous size distribution and average diameter of 1.1 nm, present in the calcined catalyst, were virtually absent in the non-modified Pd/H-Z catalyst. The corresponding palladium surface area derived from STEM (Table 1) decreased from 420 m²/g for the calcined Pd/H-Z to 70 m²/g for the spent Pd/H-Z and was roughly proportional to the activity decrease. Besides the particle sintering, degradation of the zeolite structure also contributes to the catalyst deactivation. Figure 4a shows the ²⁷Al MAS NMR spectra of the calcined and spent Pd/H-Z. Two distinct resonances were observed at chemical shifts of around 0 and 55 ppm, the former signal corresponding to the framework-associated octahedral aluminum (Al_{oct}) typical of zeolites in the H-form and the latter to the tetrahedral framework aluminum (Al_T).⁵² The spent catalyst exhibited broadening and shift to lower values of the Al_T resonance as a result of the enhanced disorder in the framework aluminum.⁵³

Previously, the complete exchange of the residual proton sites of Pd/zeolite by sodium was shown to improve significantly the stability of the catalyst by preventing both zeolite dealumination and palladium nanoparticle sintering.⁴⁶ However, the sodium-neutralized catalyst (Pd/Na-Z) displayed even lower activity and stability than Pd/H-Z, becoming completely inactive after 20 h on stream (Figure 2a). STEM images of the calcined and spent Pd/Na-Z (Figure 3c,d) show that palladium nanoparticles initially exhibited a larger average diameter (3.5 nm) than in Pd/H-Z (1.1 nm), which is in agreement with previous observations.^{46, 54} In contrast to Pd/H-Z, where the activity was proportional to the palladium specific surface area derived from STEM (Table 1), the palladium specific surface area of the spent Pd/Na-Z (70 m²/g) was only about 1.7 times lower than that of the calcined Pd/Na-Z (120 m²/g), whereas methane conversion decreased from 60% to 1%. This suggests that some other factor, besides the particle size, defines the activity and stability of the fully sodium-exchanged Pd/ZSM-5 catalysts.

3.2. Performance of Pd/H-ZSM-5 and Pd/Na-ZSM-5 after acid modification

Figure 2a illustrates the effect of various acid treatments on the catalytic activity of Pd/H-ZSM-5 and Pd/Na-ZSM-5. The activity and stability of Pd/Na-ZSM-5 after modification by acids improved compared to the non-treated Pd/Na-Z and increased in the series Pd/Na-Zc < Pd/Na-Zn < Pd/Na-Zo < Pd/Na-Zno. ICP-OES analysis of the samples (Table 2) shows that acid treatments generally resulted in a modest increase of the Si/Al ratio. Nitric acid removed aluminum most efficiently, resulting in the increase of the Si/Al ratio from 11.8 to 14.4. Oxalic and hydrochloric acids were less efficient and increased the Si/Al ratio to 13.4 and 13.3, respectively. No obvious correlation was found between the catalytic activity of dealuminated Pd/Na-ZSM-5 catalysts and the extent of dealumination. Moreover, the sample treated with oxalic acid (Pd/Na-Zo) performed significantly better than the one treated with HCl (Pd/Na-Zc), despite the same Si/Al ratio (Figure 2). Interestingly, methane oxidation activity over Pd/Na-ZSM-5 catalysts positively correlated with the final formal cation exchange level (Table 2). It is claimed that the high exchange capacity of the zeolite can promote the performance of Pd/zeolite catalysts.⁵⁵ The exchange level value was below 100% in all cases, suggesting that some aluminum species form sites, which are non-exchangeable with sodium, and that the amount of these non-exchangeable sites varies from sample to sample. Such difference in the zeolite exchange capacity can be explained by the different aluminum speciation in the samples, since this element can exist both as framework and extra-framework species in the zeolite.⁵⁶⁻⁵⁸ The former forms a cation-exchange site, whereas the role of the latter is less clear. It can be located elsewhere in the zeolite, including the external surface, or it can form a non-exchangeable site.⁵⁹⁻⁶⁰ These species can also function as a cation, occupying ion-exchange sites of the zeolite.⁶¹⁻⁶⁴

Figure 4b shows the ²⁷Al MAS NMR spectra of calcined Pd/Na-Z, Pd/Na-Zc, Pd/Na-Zn and Pd/Na-Zo. The spectra of the samples washed with nitric (Pd/Na-Zn) and oxalic acid (Pd/Na-Zo) exhibited sharper Al_T resonance (55 ppm) and a decreased contribution from distorted tetrahedrally coordinated aluminum and extra-framework aluminum at lower chemical shift (50-20 ppm) compared to Pd/Na-Z, indicating that acid treatment removed preferentially defect aluminum species from the zeolite.⁵³ On the contrary, no significant difference was observed after pretreatment with hydrochloric acid (Pd/Na-Zc). This difference in the state of aluminum, when correlated with the activity of Pd/Na-ZSM-5 catalysts, suggests that their activity and stability can be improved by the extraction of defect aluminum sites. Whereas this argument is sufficient to explain the behavior of Pd/Na-Zo and Pd/Na-Zc, alone it cannot fully explain the difference between Pd/Na-Zn and Pd/Na-Zo: the former catalyst exhibits the sharpest Al_T resonance and a higher Si/Al ratio, while the latter is more active and stable.

This observation suggests that extraction of specific aluminum species by an acid (selective dealumination) might be more important than the overall amount of removed aluminum from the sample.

Transmission IR spectroscopy was used to evaluate the presence of hydroxyl groups (Al-OH) on aluminum species, silanol groups (Si-OH) and the effect of acid treatments on the intensity of the corresponding signals.^{52, 57-58} The non-modified Pd/Na-Z exhibited three major bands in the 3200-3800 cm⁻¹ spectral region. The first band at 3743 cm⁻¹ corresponds to the terminal Si-OH groups on the external zeolite surface, the band at 3664 cm⁻¹ represents the vibrational mode of Al-OH groups and the broad band at 3520 cm⁻¹ the H-bonded Si-OH groups, the so-called “silanol nests”. Modification with hydrochloric acid (Pd/Na-Zc, Figure 5a) caused an increase in the band intensities of both external terminal Si-OH groups (3743 cm⁻¹) and H-bonded Si-OH groups (3520 cm⁻¹). These species were likely formed upon the removal of the framework aluminum from the external surface and from the bulk (from the micropores) of the zeolite, respectively.⁵² No obvious change in the amount of Al-OH groups was detected (3664 cm⁻¹) indicating that hydrochloric acid did not remove aluminum associated with Al-OH. Modification with oxalic acid (Pd/Na-Zo, Figure 5c) produced an increase in the signal corresponding to the external terminal Si-OH groups (3743 cm⁻¹). Since the amount of the H-bonded Si-OH groups (3520 cm⁻¹) changed only slightly, it can be concluded that oxalic acid preferentially removed aluminum from the external surface of the zeolite, which is in agreement with previous studies.⁴²⁻⁴³ The signal of Al-OH species at 3664 cm⁻¹ also decreased, indicating their partial removal by oxalic acid. Similarly, pretreatment with nitric acid (Pd/Na-Zn, Figure 5b) resulted in virtually complete removal of Al-OH (3664 cm⁻¹), which was accompanied by only a slight increase in the signal of the external terminal Si-OH groups (3743 cm⁻¹), suggesting that modest surface dealumination occurred. A decrease in the signal of the “silanol nests” (3520 cm⁻¹) can be explained by the dissolution of framework silicon at low pH, which is known to produce mesopores and to remove some of the H-bonded Si-OH groups.⁴⁰ Due to this effect, it is not possible to identify, whether bulk framework dealumination of the zeolite occurred in the case of Pd/Na-Zn, but the highest final Si/Al ratio of this sample suggests that nitric acid likely caused significant bulk dealumination of the framework.

Table 2 summarizes the effects of various acid modifications based on the combined data from IR spectroscopy, ²⁷Al MAS NMR and ICP-OES. Hydrochloric acid caused non-selective framework dealumination and did not remove EFAL (NMR, IR); nitric acid dissolved distorted tetrahedral aluminum (NMR), silanol nests and partly washed away EFAL

(IR); and oxalic acid led to selective surface framework dealumination and to a partial removal of EFAL (IR). Combining these conclusions with the catalytic performance of Pd/Na-Z, Pd/Na-Zc, Pd/Na-Zn and Pd/Na-Zo (Figure 2a) it can be argued that aluminum associated with Al-OH (IR), distorted tetrahedral aluminum (NMR), and the surface framework aluminum (IR) have a detrimental effect on the activity and stability of Pd/Na-ZSM-5 catalysts, while their bulk Si/Al ratio is less important. These conclusions are supported by the combined effect of dealumination by nitric and oxalic acids (Pd/Na-Zno), which resulted in an even more active and stable catalyst (Figure 2a). The removal of both EFAL and surface framework aluminum by oxalic acid was complemented by elimination of defect framework aluminum and reduction of a certain amount of silanol groups by nitric acid (Figure 5c). The Si/Al ratios of Pd/Na-Zn, Pd/Na-Zo and Pd/Na-Zno confirm that even a larger amount of aluminum was extracted from Pd/Na-Zno compared to the individual acid treatments, supporting the conclusion that oxalic and nitric acids removed different aluminum species.

The zeolite modification by an acid did not affect the performance of the catalysts in the proton form: Pd/H-Zno and Pd/H-Z exhibited very similar deactivation behavior (Figure 2a). This further supports the previous statement (see section 3.1) that deactivation mechanisms of Pd/H-ZSM-5 and Pd/Na-ZSM-5 are distinct. Whereas the dominant deactivation mechanism in Pd/H-ZSM-5 is sintering of palladium nanoparticles, Pd/Na-ZSM-5 is more sensitive to the properties of the support, notably the aluminum speciation and distribution, and the amount and location of defect sites (Si-OH groups). Alkali and alkali-earth metal oxides are well-known poisons for oxidation catalysts.⁶⁵⁻⁶⁶ Whereas sodium cations located at Brønsted exchange centers of the zeolite do not affect the reactivity of palladium-based catalysts,⁴⁶ excess of Na⁺ or Al³⁺ cations, which are not attached to the framework could cause chemical poisoning of palladium resulting in complete loss of activity of the catalyst, as observed in the case of Pd/Na-Z catalyst (section 3.1), and by adding an excess of sodium to Pd/Na-MOR catalyst as shown previously.⁴⁶ Additionally, palladium sintering still occurred in the acid-pretreated zeolite, as evinced by the STEM images of the calcined and spent Pd/Na-Zno (Figure 3e,f). The palladium surface area derived from STEM reported in Table 1 decreased more than twofold, from 280 to 110 m²/g. This indicates that although the control of aluminum distribution in Pd/Na-ZSM-5 is critical for improving the activity and stability, it is clearly not enough to achieve stable catalyst operation, and that other strategies are needed to successfully prevent Pd particle sintering.

3.3. Effect of desilication on the stability and location of palladium in Pd/Na-ZSM-5

Figure 2a shows that the catalytic activity and stability of consecutively desilicated and dealuminated Pd/Na-Dno were significantly improved compared to the samples that underwent only dealumination. Clearly, Pd/Na-Dno exhibited superior sintering-resistance: no difference in palladium particle size distribution and palladium surface area were detected by STEM after aging in reactive feed for 20 h (Figure 3g,h, Table 1). The X-ray diffraction patterns of Pd/Na-Z, Pd/Na-Zno and Pd/Na-Dno (Figure S1) indicated that after desilication all zeolite reflections exhibited the same intensity as in the starting material, suggesting no change in the crystalline nature of the zeolite. ^{27}Al MAS NMR spectra of the fresh and spent Pd/Na-Zno (Figure 4c) exhibited a decrease in the intensity of the resonance corresponding to the framework aluminum (55 ppm) and a shift to lower values, indicating a loss of framework aluminum and an increase in its distortion. On the contrary, no significant difference in the spectrum of Pd/Na-Dno was observed before and after reaction (Figure 4d), implying that the stability of the framework tetrahedral aluminum was enhanced after desilication. Additionally, consecutive treatment with base and acid allowed for more complete removal of EFAL species, which were not efficiently washed away with acids only, as inferred from the 3664 cm^{-1} band of transmission IR spectrum of Pd/Na-Dno (Figure 5d).

Figure 6a shows the argon physisorption isotherms of Pd/Na-Dno and Pd/Na-Z. Whereas the argon uptake did not change in the microporous region (below 0.1 p/p_0), a notable rise in the adsorption occurred at higher relative pressures. The pore size distribution (Figure 6b), obtained from fitting the argon physisorption isotherm using the non-local density functional theory model for zeolites (NLDFT),⁶⁷⁻⁶⁸ revealed the presence of mesopores ($17\text{ m}^2/\text{g}$) in the non-pretreated material (Pd/Na-Z), which was assigned to the roughness of the external surface of the zeolite. The distributions obtained for Pd/Na-Zc, Pd/Na-Zn and Pd/Na-Zo suggest that individual acid pretreatments did not produce any additional porosity (Figure 6, Table S1) in the zeolite. Desilication produced additional mesopores (Table S1) with the pore diameter ranging from 2 to 10 nm (Pd/Na-Dno, Figure 6). The generation of these internal defects in Pd/Na-Dno was also confirmed by the appearance of a new signal in the transmission IR spectrum (Figure 5d) corresponding to the internal terminal Si-OH groups (3729 cm^{-1}),⁵² which was not present in the acid pretreated samples (Figure 5a-c). More mild base treatment (0.1 M) neither affected the pore structure of the catalyst nor improved its performance (Figure S2), whereas more severe desilication (0.5-0.8 M) still improved the catalyst stability, but decreased its activity.

Scanning transmission electron microscopy was employed to locate palladium species in spent Pd/Na-Zno and spent Pd/Na-Dno. The comparison of secondary and transmission electron images of spent Pd/Na-Zno (Figures 7a and 7b, respectively) reveals that most of palladium nanoparticles occurred on the external surface of the zeolite, whereas in the case of spent Pd/Na-Dno the nanoparticles were located predominantly within the zeolite (Figure 7c,d). The higher stability of Pd/Na-Dno compared to other catalysts is thus achieved by the three effects of desilication: more complete removal of EFAL, stabilization of the framework aluminum and encaging of palladium nanoparticles in the constrained intracrystalline mesopores. This led to the physical separation of the well-dispersed active phase and prevented sintering, resulting in superior stability and high activity, even in the presence of steam, which is known to promote palladium aggregation.^{13, 19-20}

3.4. Generalization of results

The described synthetic approach can be applied to other zeolite structures as can be seen from the performance of non-modified, dealuminated and consecutively base-acid treated Pd/Na-BEA (Figure 2b) and Pd/Na-MOR (Figure 2c). Since some zeolite frameworks can exhibit different susceptibility to acid and base treatments, the post synthesis modification conditions for the zeolite beta had to be adjusted,⁶⁹ whereas for mordenite and ZSM-5 an identical synthesis protocol was used. Similar to ZSM-5 (Section 3.1), neutralization of non-modified Pd/BEA by sodium resulted in an unstable catalyst, which lost the activity completely after 20 h on stream, while mildly dealuminated Pd/Na-BEA-o and consecutively desilicated and dealuminated Pd/Na-BEA-Do showed enhanced activity and stability. Similar trends were observed for Pd/Na-MOR, which after base-acid treatment showed exceptional stability for over 80 h in the presence of steam (Figure 2c) and remained active even after hydrothermal ageing at 600°C (Figure S3). Finally, the stability and activity of Pd/zeolite catalysts prepared using the novel synthesis route do not depend on the type of charge-balancing cation (Na^+ , K^+ and Cs^+) as shown for Pd/MOR-no (Figure S4). Therefore, at least three various zeolite framework types (MFI, BEA and MOR) exhibit similar behavior when consecutively loaded with palladium and a monovalent alkali cation. This implies that the presented synthetic approach is generally applicable to Pd/zeolite systems and can potentially be exploited for other reactions.

Table 3 summarizes the causes of metal zeolite-based catalyst deactivation and synthesis measures that can be taken against it. While acidity-induced Ostwald ripening can be mitigated by either alkali titration of the acid sites or use of high-silica support (associated

with the difficulty of active metal impregnation), nanoparticle aggregation can be prevented by introducing a secondary network of constricted mesopores, which isolate them from each other. Finally, the active metal may be blocked or poisoned by extra-framework species, which can be initially present in the support or occur due to degradation of defect framework areas under reaction conditions. These species can be efficiently removed by selective dealumination.

4. Conclusions

We demonstrated a novel approach to the synthesis of sintering-resistant Pd/zeolite catalysts and proved its efficiency in the demanding methane oxidation reaction. Whereas deactivation of conventional Pd/H-ZSM-5 catalysts is governed by sintering of palladium nanoparticles, the performance of the fully-exchanged Pd/Na-ZSM-5 catalysts is sensitive to the aluminum speciation and distribution in the zeolite. Selective removal of extra-framework, surface framework and defect framework aluminum by pretreating the zeolite with a mixture of oxalic and nitric acids allowed to improve significantly the activity and stability of Pd/Na-ZSM-5. However, such catalysts continued to deactivate through palladium sintering. Desilication prior to acid dealumination allowed to more efficiently remove extra-framework aluminum and produced mesopores, which served as containers for small palladium nanoparticles, thus physically separating these entities from each other and preventing their growth. In addition to the aluminum distribution and pore structure, stability of the zeolite is an important factor. Consecutive desilication and dealumination removed primarily defect areas of the zeolite and thus gradually improved the stability of the framework aluminum, which helped to further enhance the performance of the catalyst. After adjustment of the synthesis conditions, the approach can be applied to other zeolite structures, for instance, zeolite beta and mordenite. The results show that there is a great potential for improving the efficiency of metal zeolite catalysts by rational post-synthetic modification of the support material.

Supporting Information. Textural properties of calcined Pd/ZSM-5 catalysts; XRD patterns of selected Pd/ZSM-5 catalysts; methane conversion over desilicated Pd/ZSM-5 samples; methane conversion on Pd/Na-MOR-Dno before and after hydrothermal ageing and on Pd/Na-MOR-no, Pd/K-MOR-no and Pd/Cs-MOR-no.

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Competing interests

The authors declare no competing interest.

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Figure 1. Overview of the various post-synthesis modifications of ZSM-5 (Clariant SM-27, Si/Al=13, H-form, calcined at 500 °C for 2 h). Zeolite modification was carried out prior to palladium and sodium exchange. Acid treatments were performed at 80 °C under reflux for 4 h. Base treatment was performed at 65 °C for 30 min.

Figure 2. Methane conversion over (a) Pd/ZSM-5, (b) Pd/Na-BEA and (c) Pd/Na-MOR. Conditions: 1 vol.% CH₄, 4 vol.% O₂, 5 vol.% H₂O, bal N₂, 410 °C. Steam was added to the feed at t = 0.

Figure 3. Scanning transmission electron micrographs (STEM) and the corresponding palladium particle size distributions of (a,b) fresh and spent Pd/H-Z, (c,d) fresh and spent Pd/Na-Z, (e,f) fresh and spent Pd/Na-Zno and (g,h) fresh and spent Pd/Na-Dno, respectively. Distributions were obtained from the analysis of 12 STEM images of each sample. Spent catalysts have been aged in a flow containing 1 wt. % CH_4 , 4 vol. % O_2 , 5 vol. % H_2O , bal N_2 at 420 °C for 20 h.

Figure 4. ^{27}Al MAS NMR spectra of (a) calcined and spent Pd/H-Z, (b) calcined Pd/Na-Z, Pd/Na-Zc, Pd/Na-Zo and Pd/Na-Zn, (c) calcined and spent Pd/Na-Zno and (d) calcined and spent Pd/Na-Dno.

Figure 5. Transmission IR spectra of variously modified Pd/Na-ZSM-5 catalysts. The spectra are offset for clarity and are compared to the spectrum of Pd/Na-Z as the reference.

Figure 6. (a) Argon physisorption isotherms of Pd/Na-Z and Pd/Na-Dno and (b) differential pore volume of the non-pretreated and variously pretreated Pd/Na-ZSM-5 catalysts.

Figure 7. Secondary electron image of (a) spent Pd/Na-Zno and (c) spent Pd/Na-Dno, scanning transmission electron image of (b) spent Pd/Na-Zno and (d) spent Pd/Na-Dno. Detection of secondary electrons allows the selective analysis of the external surface of the sample, while the transmitted electrons of the scanning electron image probe the whole sample depth and is thus ambiguous on the location of the nano-particles.

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Table 1. Palladium average particle size and surface area derived from STEM

Sample	Average Pd particle diameter, nm		Pd surface area from STEM, m ² /g		Methane conversion ^a , %	
	calcined	spent	calcined	spent	calcined	spent
Pd/H-Z	1.1	3.1	420	70	60	10
Pd/Na-Z	3.5	5.1	120	70	60	1
Pd/Na-Zno	2.1	3.6	280	110	80	62
Pd/Na-Dno	2.4	2.6	270	280	79	83

^aconditions: 1 vol.% CH₄, 4 vol.% O₂, 5 vol.% H₂O, N₂ bal. 420 °C.

Table 2. Chemical composition of Pd/ZSM-5 catalysts and effect of post-synthesis modifications of the zeolite.

Sample	Si/Al ratio	Pd, wt. %	Na, wt. %	Formal exchange level ^a , %	EFAL ^b , a.u.	Effect of post-synthesis modifications
Pd/H-Z	11.8	0.98	< 0.01	15	—	—
Pd/H-Zno	14.6	0.97	< 0.01	19	—	—
Pd/Na-Z	11.9	0.89	1.8	81	4.9	—
Pd/Na-Zc	13.3	0.96	1.6	84	4.2	bulk dealumination
Pd/Na-Zn	14.4	0.91	1.8	93	1.7	bulk dealumination, dissolution of Si-OH groups
Pd/Na-Zo	13.4	0.89	1.8	91	1.7	surface dealumination
Pd/Na-Zno	15.0	0.96	1.7	88	1.6	surface and bulk dealumination, dissolution of Si-OH groups
Pd/Na-Dno	14.8	0.92	1.7	93	0.6	formation of mesopores, surface and bulk dealumination, dissolution of Si-OH groups

^acalculated using the formal equation $(2 \times n_{Pd} + n_{Na})/n_{Al}$, assuming Pd²⁺ species.

^bobtained from integrating peak at 3664 cm⁻¹ of IR spectra shown in Figure 5.

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Table 3. Causes for metal-zeolite catalyst deactivation and countering synthetic strategies

Deactivation cause	Synthesis modification	Effect
Ostwald ripening induced by support acidity	titration of acid sites with alkali ⁴⁶ or use of high-silica zeolite ¹²	removal of acid sites
metal particle agglomeration	mild desilication	isolation of nanoparticles in constricted mesopores
self-poisoning by extra-framework species	selective dealumination	removal of extra-framework and defect framework species

Table of Content graph