Grafting of Alkali Metals on Fumed Silica for the Catalytic Dehydrogenation of Methanol to Formaldehyde

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Water free, non-oxidative catalytic dehydrogenation of methanol to formaldehyde is an important process for the formation of anhydrous, molecular formaldehyde (FA). Sodium or sodium-containing salts were shown to catalyze the reaction, but their reaction mechanism remains unclear. In this work, we thus investigated the performance of a series of catalysts prepared by grafting of alkali metals on amorphous silica for methanol catalytic dehydrogenation. The resulting catalysts displayed an increased activity for the catalytic dehydrogenation of methanol. Variation of the electron density of the supported alkali metal cations severely affected the FA selectivity, which followed the trend: Li > Na > K > Rb > Cs. A large gap in selectivity towards FA between ions with a high (i.e., Li, Na) and low charge density (i.e., K, Rb, Cs) was observed. Also, increased metal loading adversely affected FA selectivity and resulted in a larger production of carbon monoxide. Sodium grafted on silica yielded the best combination of moderate conversion and high selectivity.

1. Introduction

With a yearly production volume of millions of tons per year, formaldehyde (FA) is a base chemical in the industry for many materials such as resins, polymers, paints or explosives.[1] It is the simplest aldehyde and a highly reactive organic compound. It is commercially available as an aqueous solution containing 37 to 55 wt% FA with methanol residues from the FA synthesis process, which inhibits the formation of insoluble polymers.[2] Current FA production processes rely on the oxidative dehydrogenation of methanol over silver or iron-molybdenum catalysts, which results in the formation of large quantities of water as by-product.[3] All industrial processes use a combination of non-oxidative [Eq. (R1)] and oxidative methanol dehydrogenation [Eq. (R2)].[3]

\[
\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2; \Delta H^\circ = +84 \text{kJ/mol} \quad \text{(R1)}
\]

\[
\text{CH}_3\text{OH} + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}; \Delta H^\circ = -159 \text{kJ/mol} \quad \text{(R2)}
\]

By performing the reaction under anaerobic conditions, the oxidative dehydrogenation of methanol can be suppressed, in favor of the non-oxidative methanol dehydrogenation to FA and hydrogen (here referred to as anhydrous catalytic methanol dehydrogenation).[4] Despite appearing as relatively straightforward, anhydrous catalytic methanol dehydrogenation is a challenging reaction: high temperatures are required to overcome the large positive enthalpy of reaction and sufficient methanol conversion can only be reached at temperatures above 600°C.[5,6] FA is unstable at these temperatures and several side reactions diminish the overall reaction yield (e.g., FA decomposition to carbon monoxide (CO) and methanol dehydration to dimethyl ether).[7]

Anhydrous catalytic methanol dehydrogenation to FA is not a novel approach. Several research studies have addressed this reaction before.[5,7–9] But this process never reached the industrial scale, although a few patents applications have been published.[10,11] However, the recent development of oxymethylene dimethyl ether (OME) as potential fuel has renewed interest in this reaction.[12] OME can be produced sustainably, when using methanol from renewable sources together with anhydrous FA for its synthesis.[13–15] As the presence of water can severely hinder reactions kinetics to produce OME from FA, an anhydrous source of FA (i.e., trioxane) is favored to obtain fast reaction kinetics and limit the amount of byproducts.[16] Anhydrous catalytic methanol dehydrogenation to produce monomeric, anhydrous FA was shown as a feasible and cost-efficient alternative to trioxane and its energy-intensive synthesis process.[15,16] Furthermore, hydrogen is a valuable byproduct of this reaction and is also considered as a clean transportation fuel of the future.

Many research studies have been dedicated to the identification of suitable catalysts for anhydrous catalytic methanol dehydrogenation since the 1960s. The reviews from Su et al. and Usachev et al. provide an overview of the catalyst candidates that were hitherto investigated.[5,15] Silver-based catalysts demonstrated high activity but relied on the presence of surface oxygen, and bulk oxygen present in the silver lattice, resulting in the production of water as side-product.[20] They were shown to deactivate rapidly in the absence of oxygen and

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required frequent regenerations by oxidative treatments.[21] Copper possesses a high selectivity for the dehydrogenation of alcohols but a low specific activity. Research on Cu-containing catalyst has therefore focused on finding effective supports and modifiers.[19] Phosphorous was found to increase significantly the catalyst activity when it is supported on silica and the highest recorded yield was in the 40% range at temperatures between 400 and 500°C for a CuO–Cu(PO₄)₂/SiO₂.[22] This performance could not be reproduced by other researchers and the catalyst was prone to rapid deactivation.[23] Zinc-based catalysts were also found to be active for the catalytic dehydrogenation of methanol and were studied extensively over various supports. Under mild conditions, up to 50% conversion was reported with a FA selectivity of 90% over a ZnO/SiO₂ catalyst.[24] Yet, irreversible catalyst deactivation occurred under typical reaction conditions due to reduction of ZnO and subsequent evaporation of metallic zinc.[25] Unfortunately, quantification of the water level in the product stream from anhydrous catalytic methanol dehydrogenation is generally not reported in the literature. It is assumed that this due to the trace amount of water in the product stream and the difficulty to quantify the water level using gas chromatography.

Another group of catalysts active for anhydrous catalytic methanol dehydrogenation are alkali metals.[3] Amongst these elements, sodium was studied in various forms (e.g. sodium carbonate, sodium aluminates) and demonstrated the highest activity compared to other studied catalysts.[26] The mechanism of the methanol dehydrogenation reaction on sodium-based catalysts remains unclear. It was suggested that dissociative adsorption of methanol occurred on siloxane bridges of a Na-ZSM-5 zeolite.[22] Other authors proposed that the reaction is initiated at the surface of the catalyst, and then proceeds in the gas-phase.[28] It was also reported that hydrogen desorption was the rate-limiting step, which could be accelerated by hydrogen spillover on active carbon.[28] Sauer et al. also demonstrated that alkali salts decompose at high temperatures leading to sodium evaporation, which then induces a homogeneous radical vapor-phase reaction.[29,30] Alkali metals present as ions in zeolite X or Y were also used in the side-chain alkylation of toluene with methanol, which requires dehydrogenation of methanol to FA as an intermediate step.[31,32]

Alkali metals possess an important potential to catalyze the catalytic dehydrogenation of methanol, but it remains unclear why sodium is the most active among these elements. Moreover, there is a need for the development of stable catalysts, which can prevent sodium evaporation while preserving its activity towards catalytic dehydrogenation of methanol. For this purpose, we used amorphous silica as a support to graft alkali metals according to a method developed by Keller et al.[33] During this procedure, surface sites such as silanol groups are deprotonated to silanolates under basic conditions, followed by ion-exchange with an alkali metal (Scheme 1). This method can achieve atomic dispersion while preventing amorphization of the support by inhibiting Si–O bond hydrolysis.[33,34]

Silica was chosen as a support due to its high thermal stability, inertness, and mechanical strength. The use of other supports that have acidic surface groups, such as Al₂O₃, was not considered as their use can lead to methanol dehydration and coke formation.[3,21] The goals of this study were two-fold: First, we aimed to assess the catalytic performance of each of the synthesized catalysts. Second, we intended to achieve a deeper understanding of the structure-activity relationship of alkali metal-grafted silica for the catalytic dehydrogenation of methanol.

2. Materials and methods

2.1. Preparation of alkali metal supported on fumed silica

All reagents were of analytical grade and obtained from commercial suppliers. No further purification was applied unless specified. Alkali metals grafted on silica were prepared according to a protocol developed by Keller et al.[33] Typically, Aerosil®-fumed silica was dried overnight in an oven at 150°C. It was then transferred to a round bottom flask under inert atmosphere using Schlenk techniques. The calculated amount of the alkali metal hydroxide salt (LiOH, ADR, 98%; NaOH, Sigma-Aldrich, 97%; KOH, Fisher Chemicals, 85%; RbOH·2H₂O, Fluka, 95%; CsOH 50 wt% in H₂O, ADR, 99.9%) was inserted in another round bottom flask, in which methanol (anhydrous, Sigma-Aldrich, 60 mL·g⁻¹ of silica) was transferred by cannula transfer. Following complete salt dissolution, the methanolic solution was transferred to the round bottom flask containing the silica powder. The mixture was then stirred by magnetic stirring (450 rpm) at 25°C for 10 min. After quenching with ice, it was filtered and washed with methanol (3 times with ca. 100 mL). The powder was then dried overnight at 110°C. Finally, it was calcined in static air at 550°C with a temperature ramp of 10°C·min⁻¹.

![Scheme 1. Grafting of alkali metals on fumed silica according to Keller et al.[33]](image-url)
The different catalysts were designated as M–SiO$_2$, where M is the alkali metal used during grafting. If not mentioned otherwise, a 0.1 M MOH concentration in methanol was used during grafting. A second series of catalysts was synthesized with a smaller metal loading and is referred to as M–SiO$_2$–SL. During the grafting procedure of these samples, the concentrations of KOH, RbOH and CsOH in methanol were 3.75·10$^{-2}$, 1.88·10$^{-2}$ and 9.37·10$^{-3}$ M, respectively. For the Na-grafted catalysts, the concentration was varied from 0.05 to 0.15 M and the resulting samples are referred to as Na–SiO$_2$–xM, where x is the concentration of NaOH during grafting. Finally, grafting in isopropanol (IPA, anhydrous, Sigma-Aldrich) was also performed with a 0.1 M NaOH concentration, resulting in the sample M–SiO$_2$–IPA. The extent of amorphization $\xi_{amorph}$ of a sample was defined according to Equation (R3), where $S_{BET}$ (SiO$_2$) and $S_{BET}$ (sample) are the specific surface area of silica and of the sample after the grafting procedure, respectively.

$$\xi_{amorph} = \frac{S_{BET}(SiO_2) - S_{BET}(sample)}{S_{BET}(SiO_2)}$$  \hspace{1cm} \text{(R3)}$$

### 2.2. Material Characterization

N$_2$ physisorption experiments were performed on a Micrometrics 3Flex apparatus at liquid nitrogen temperature and N$_2$ relative pressures between 0.1 and 0.99. Typically, ca. 150 mg of the samples were dried at 120°C (temperature ramp 5°C/min) for 5 h. A leak test was performed before the analysis. Brunauer-Emmett-Teller (BET) surface, Barrett-Joyner-Helenda (BJH) and t-plot method were used to calculate the specific surface area, the mesoporous and microporous volume, respectively. Elemental analyses were performed using inductively coupled plasma optical emission spectrometry (ICP-OES) at the Paul Scherrer Institute on a Vista pro AX Varian instrument. Silica samples were dissolved in a 10 mL aqueous solution containing 0.5 mL of 40% hydrofluoric acid, 0.5 mL of 65% nitric acid and 0.25 mL of 30% hydrochloric acid for 2 h at 95°C. XPS spectra were measured on a PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany) with a monochromatic Al K$\alpha$ X-ray source of 24.8 W power and 100 µm beam size. The measurement accuracy of the instrument was of 0.1 eV.

X-ray diffraction (XRD) patterns were recorded using a D8 advance Bruker optical emission spectrometry with a 1D-LynxEye detector (Cu K$\alpha$ radiation, no monochromator, Ni filter). A step size of 0.01 was used. The structure of the sample was checked by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) on a FEI Tecnai Osiris with 200 kV acceleration voltage. Grids were prepared by deposition of a drop of sample suspension on a Lacey carbon grid.

CO$_2$ temperature-programmed desorption (CO$_2$–TPD) experiments were performed on a Micromeritics Autochem 2920 II instrument. The sample (0.15 g) was first dried during 2 h at 550°C using a 50 mL·min$^{-1}$ flow of He at 10°C·min$^{-1}$ heating rate. Then, the sample was saturated with a continuous flow (50 mL·min$^{-1}$) of CO$_2$ at 50°C, followed by a purge step using He (50 mL·min$^{-1}$) for 1 h at the same temperature to remove physisorbed CO$_2$. Afterwards, the desorption of CO$_2$ was monitored by an MKS Cirrus II mass spectrometer (mass 44) between 50 and 700°C. Finally, three injections of a known volume of CO$_2$ were used for calibration of the MS signal.

Methanol temperature-programmed desorption (methanol-TPD) was performed using the set-up described in section 2.3. For the measurements, 150 mg of catalyst was dried under a 50 mL·min$^{-1}$ flow of Ar at 650°C (10°C·min$^{-1}$), until no more water was detected in the reactor outlet. The reactor temperature was then lowered to 350°C and the sample was saturated with methanol for 60 min with a 100 mL·min$^{-1}$ Ar flow (1.5% methanol). While maintaining the methanol flow, the temperature was lowered to 50°C and the saturation continued for 1 h once 50°C were reached. Afterwards, the sample was purged with a 50 mL·min$^{-1}$ flow of Ar to remove physisorbed methanol. The sample temperature was then raised to 800°C (10°C·min$^{-1}$) and the desorption profiles of methanol, FA and CO were monitored with the online FTIR.

### 2.3. Catalytic testing

Dehydrogenation of methanol was performed using the experimental set-up shown in Scheme S1. Argon was used as the carrier gas and methanol was introduced in the feed via a methanol bubbler (a). The reaction was performed in a 10 mm quartz-tube, fixed bed reactor (b) with a heating element allowing the temperature to reach 800°C. Quartz wool was used to support the catalyst and to ensure proper gas mixing. The gas flows were calibrated using a bubble flowmeter (c). Gas compositions were analyzed using an online Fourier transform infrared spectrometer (FTIR) Bruker Matrix MG-01 FTIR (d), equipped with a 10 cm gas cell heated at 120°C. The OPUS GA software was used for quantification of the gas composition based on the collected IR spectra.

The catalytic tests were conducted in a 10 mm tubular, fixed-bed reactor. For each test, the desired amount of catalyst was weighted, loaded in the reactor and fixed in place using quartz wool. Each catalyst was first dried under a 50 mL·min$^{-1}$ Ar flow at 650°C using a temperature ramp of 10°C·min$^{-1}$, until no more water was detected. The Ar flow was then switched to bypass the reactor and methanol was introduced via a bubbler thermostated at 30°C to reach 1.5% methanol in a total Ar flow of 100 mL·min$^{-1}$. The flow was fed into the reactor when the methanol concentration was stable. The reactor was working at atmospheric pressure for all catalytic tests.

Methanol conversion ($X_{\text{MeOH}}$), selectivity towards FA ($S_\text{FA}$) and yield of FA ($Y_\text{FA}$) were used to compare the performance of each catalyst sample. They were defined as Equations (R4)–(R6):

$$X_{\text{MeOH}} = \frac{|\text{MeOH}]_\text{in} - |\text{MeOH}]_\text{out}|}{|\text{MeOH}]_\text{in}}$$ \hspace{1cm} \text{(R4)}$

$$S_\text{FA} = \frac{|\text{FA}]_\text{out}}{|\text{MeOH}]_\text{in}}$$ \hspace{1cm} \text{(R5)}$

$$Y_\text{FA} = \frac{|\text{FA}]_\text{out}}{|\text{MeOH}]_\text{in}}$$ \hspace{1cm} \text{(R6)}$
To ensure that all reaction products were monitored, the carbon balance was calculated for each experiment according to Equation (R7):

\[ C_{\text{balance}} = [\text{MeOH}]_{\text{out}} + [\text{FA}]_{\text{out}} + 2[DME]_{\text{out}} + [\text{CO}_2]_{\text{out}} + [\text{CO}]_{\text{out}} + [\text{CH}_4]_{\text{out}} \quad (\text{R7}) \]

To regenerate the catalyst activity after coking, temperature-programmed oxidation (TPO) experiments were performed in situ using the following method: The sample temperature was decreased to 300 °C under an Ar flow of 50 mL·min⁻¹, followed by synthetic air (40 mL·min⁻¹). Once no desorbed products were detected at this temperature, the sample temperature was raised to 700 °C at a heating rate of 10 °C·min⁻¹. After TPO and before the next catalytic test, the sample was purged at 650 °C with an Ar flow of 50 mL·min⁻¹.

### 3. Result and discussion

#### 3.1. Physico-chemical characterization of the catalysts

The elemental composition of each catalyst was investigated by ICP-OES (Figure 1, Table 1). The results confirmed that all alkali metals were successfully supported on silica. The metal content of the catalysts, which were supported using an alkali hydroxide concentration of 0.1 M varied significantly across the various alkali metals. An approx. fourfold increase was found in the metal to silicon (M : Si) molar ratio between Li–SiO₂ (0.0021) and Na–SiO₂ (0.0087). Moving down the group 1 elements of the periodic table from Na to Cs, the M : Si ratio approximatively doubled between each element with a maximal value of 0.0769 for Cs–SiO₂. Considering that the basicity of the hydroxide salts increases with the alkali metal cation size, higher molar metal loadings were obtained with larger alkali metals.[35] Larger salt basicity resulted in a larger deprotonation of the silica surface and a larger concentration of silanolates available for ion-exchange.

In the case of Na, the grafting procedure was repeated by varying the concentration of NaOH, as well as by substitution of methanol with isopropanol. By decreasing the NaOH concen-

![Figure 1. Alkali metal to silicon molar ratio (M-Si) of the various synthesized catalysts.](image)

| Table 1. Characterization results from ICP-OES, N₂ physisorption and CO₂ chemisorption. |
|---------------------------------|---------------------------------|------------------|------------------|------------------|
| M : Si molar ratio [-]          | Surface area [m²·g⁻¹]          | Basicity [μmol CO₂·g⁻¹] |
| [a]                             | [b]                             | [c]               |
| Li–SiO₂                         | 0.0021                          | 218               | 19               | 179              | 0.90             |
| Na–SiO₂                         | 0.0087                          | 169               | 15               | 142              | 13.00            |
| K–SiO₂                          | 0.0169                          | 135               | 13               | 111              | 25.05            |
| Rb–SiO₂                         | 0.0371                          | 121               | 15               | 97               | 27.48            |
| Cs–SiO₂                         | 0.0769                          | 95                | 14               | 72               | 23.60            |
| Na–SiO₂-IPA                     | 0.113                           | 69                | 4                | 59               | 85.35            |
| Na–SiO₂-0.05                    | 0.0044                          | 170               | 14               | 148              | /                |
| Na–SiO₂-0.15                    | 0.0099                          | 157               | 15               | 133              | /                |
| K–SiO₂-SC                       | 0.082                           | 176               | 10               | 156              | 11.96            |
| Rb–SiO₂-SC                      | 0.0219                          | 166               | 13               | 139              | 13.67            |
| Cs–SiO₂-SC                      | 0.0281                          | 160               | 16               | 143              | 4.76             |

[a] Derived from the t-plot method. [b] Derived from the BJH method using the adsorption branch.
metal loading to 0.0099 for Na concentration to 0.15 M resulted in a more modest increase in solvent compared to methanol during grafting of Na, with the extent of amorphization was much higher when using IPA as in methanol resulted in lower BET surface area. Additionally, the solvent used. Overall, grafting with larger alkali metals varied according to the alkali metal, the MOH concentration, and the basicity becomes stronger.

The catalyst series produced with a lower concentration of alkali hydroxide salt resulted in less surface amorphization, which can be inferred from the comparison of the BET surface area of samples M–SiO₂ with M–SiO₂-SL. Overall, a correlation was found between the extent of sample amorphization and catalyst loading (Figure 2b), which highlights the trade-off between deposition of alkali metals on silica and preservation of its surface area. These results are in line with the findings from Keller et al.[31]

CO₂ temperature-programmed desorption (CO₂-TPD) was performed to quantify the number and strength of the basic sites of each catalyst (Figure 3a). From SiO₂, the CO₂ peak area increased when moving down the group 1 elements, which indicated the presence of basic sites following alkali metal grafting.[31] The increasing concentration of the basic sites seemed to reach a plateau: when using Cs–SiO₂ instead of K–SiO₂, the peak area did not change significantly, despite the increase in the M:Si ratio identified by ICP-OES. This could indicate that the surface became saturated with alkali metals at M:Si ratios above that of K–SiO₂ (0.0169). Alternatively, the increase in concentration of basic sites could have reached a plateau due to the combination of increasing surface loading and decreasing specific surface area. Due to their higher basicity, Rb and Cs hydroxide resulted in dissolution of a larger fraction of silica as well as higher deposition of the respective alkali metal on the silica surface. The highest basicity was obtained for Na–SiO₂-IPA with a value of 85.35 μmol CO₂·g⁻¹, considerably higher than Na–SiO₂ (13.00 μmol CO₂·g⁻¹). The basicity values obtained for the M–SiO₂-SL series where similar to that of Na–SiO₂ (±13 %), except in the case of Cs–SiO₂-SL, for which 4.76 μmol CO₂·g⁻¹ was recorded.

The nature of the alkali metal supported on silica did not appear to affect strongly the strength of the basic sites, as all the CO₂ peak maxima are located between 110 °C and 150 °C. Analysis of the binding energy of oxygen (O 1s) can provide information on the oxygen basicity: as the O 1s binding energy increase in concentration of basic sites could have reached a plateau
that the relative basic strength of each of the catalysts was similar, which was reflected by the same value of the binding energy obtained, considering the measurement accuracy of the instrument (Figure 3b).

Methanol temperature-programmed desorption (methanol-TPD) was performed, during which the desorption of methanol, FA and CO were recorded (Figure 4). Figure 4a shows two methanol desorption peaks, the first of which at about 150°C increases in area with increasing atomic number within the alkali metal group. This peak was attributed to weakly adsorbed methanol and its desorption peak maximum was at the same temperature for all alkali metals. The second peak at higher temperatures, attributed to strongly adsorbed methanol, formed due to the electrostatic interaction between the lone electron pair of the oxygen atom and the grafted alkali metals.[37] It can be observed that the position of the desorption peak maximum of the strongly adsorbed methanol decreased with increasing alkali metal size. Li–SiO$_2$ did not follow the trend, probably as a result of its smaller metal loading compared to the other samples.

FA was produced at temperatures above the desorption peak of strongly adsorbed methanol (Figure 4b). For all alkali-grafted catalysts, the amount of desorbed FA was smaller compared to the amount of desorbed methanol. The desorption peak maximum of FA also shifted to lower temperatures when moving down the alkali metals catalysts in the periodic table, except for Rb–SiO$_2$ which produced FA as from 250°C. CO was produced in more significant amount compared to FA and the minimum desorption temperature was around 350°C. Higher amounts of CO were produced for SiO$_2$ as well as Li- and
Na–SiO₂ with a desorption maximum at about 750 °C (Figure 4c). In contrast, a decreasing desorption peak maximum was observed for K–SiO₂, Rb–SiO₂, and Cs–SiO₂. It is also interesting to note that unlike to the desorption of methanol, the presence of alkali metals on SiO₂ was not necessary to produce CO.

It is difficult to assign the cause of change in desorbed products from the methanol-TPD between the different catalysts in the M–SiO₂ series because the different alkali metal hydroxide salts used at the same concentration during grafting resulted in very different M:Si ratio. Therefore, methanol-TPD was also performed on the catalysts synthesized with smaller metal loading for K, Rb and Cs (M–SiO₂–SL), and were compared to Na- and Li–SiO₂ (Figure 5). Desorption of methanol followed a similar trend, but the desorption peak for the strongly adsorbed methanol shifted less to lower temperatures compared to the M–SiO₂ samples (Figure 5a). Conversely, the desorption peaks of FA (620 °C) and CO (755 °C) were approximately the same for all samples in the M–SiO₂–SL series, unlike the M–SiO₂ series (Figure 5b and c). Considering that methanol adsorbed on the alkali metals and partial or full dehydrogenation occurred regardless of the presence of these metals, it was concluded that different sites exist on the samples.

3.2. Catalytic activity

The performance of the M–SiO₂ series of catalysts was investigated for the catalytic dehydrogenation of methanol at 650 °C (Figure 6). Compared to the unmodified SiO₂, which was relatively inactive, all grafted catalysts displayed an increased
activity for the reaction. The conversion of methanol increased as the atomic weight and the concentration of the alkali metal increased (Figure 6a). The results for the selectivity towards FA displayed an opposite trend: the most selective candidates were SiO\textsubscript{2} and Li–SiO\textsubscript{2}, followed closely by Na–SiO\textsubscript{2} (Figure 6b). A large drop in FA selectivity was observed for larger alkali metals (i.e., K, Rb, Cs), falling from 0.63 to 0.04 after 7.5 h on stream when using K instead of Na.

Overall, the highest yield was obtained for Na–SiO\textsubscript{2} with a value of 0.24 after 20 h on stream (Figure 6c). The second-best candidate was Li–SiO\textsubscript{2} due to its large FA selectivity, followed by the larger alkali metals grafted on silica. The composition of the product stream after 7.5 h of reaction is shown in Figure 6d. An increasing amount of methanol was converted to CO moving down the elements in group 1 of the periodic table. This means that complete dehydrogenation of methanol to CO was the main cause for the decrease in FA selectivity. Besides FA and CO, DME and CH\textsubscript{4} were also produced. DME production is a result of the dehydration of methanol and was accompanied by the production of water. At high temperatures, DME experiences pyrolysis to methane, CO, and hydrocarbons as well as various coke precursors.\cite{38} These side-reactions, which severely diminished the selectivity towards FA, were observed to a higher extent for larger alkali metal cations grafted on silica. Na–SiO\textsubscript{2} yielded the lowest ratio of water per product generated, which is essential in anhydrous catalytic methanol dehydrogenation.

Su et al. demonstrated that the selectivity to FA decreases when the conversion reaches values above 80%, which is close to the thermodynamic limit, due to the instability of FA at temperatures above 600 °C.\cite{5} It could be thus argued that the lower FA selectivity of K–, Rb–, and Cs–SiO\textsubscript{2} is a result of the high methanol conversions. Therefore, their performances were tested with an increased WHSV in order to reach lower conversion value (Figure S2). At 2.5 times higher WHSV, their methanol conversion was effectively reduced below 0.70 and their selectivity towards FA increased to a maximum of 0.10 for K–SiO\textsubscript{2}, which was still much lower compared to the FA selectivity of Na–SiO\textsubscript{2} at 2.5 times lower WHSV. The complete dehydrogenation of methanol to CO was still the dominant reaction pathway.

Considering that the metal loading and the nature of the alkali metal are changing simultaneously, it is difficult to attribute the change in activity to one or the other parameter using the catalytic test results from the M–SiO\textsubscript{2} catalysts series. Therefore, the same catalytic test was performed using the M–SiO\textsubscript{2}-SL catalysts series, in which the metal loadings were significantly reduced for each alkali metal (see section 2.1. and Table 1). The characterization results showed that their M:Si molar ratios were comprised between 0.0082 (K–SiO\textsubscript{2}-SL) and 0.0281 (Cs–SiO\textsubscript{2}-SL). However, the basicity of Cs–SiO\textsubscript{2} was considerably smaller than K–SiO\textsubscript{2}, with values of 4.76 and 11.96 μmol CO\textsubscript{2}·g\textsubscript{cat}\textsuperscript{-1}, respectively (Table 1).

The results of the catalytic tests with the M–SiO\textsubscript{2}-SL catalysts are compared with the reference Na–SiO\textsubscript{2} sample in Figure 7. As expected, the methanol conversion was lower for each catalyst compared to their M–SiO\textsubscript{2} counterparts, and followed the following trend: Cs–SiO\textsubscript{2} > K–SiO\textsubscript{2} > Rb–SiO\textsubscript{2} > Na–SiO\textsubscript{2} (Figure 7a). Thus, it did not exactly follow the order of the group 1 elements. However, selectivity to FA became smaller as one moves down the group 1 elements (Figure 7b). Among the grafted alkali metals, the highest FA selectivity was reached for Na (0.64), largely above K (0.19), Rb (0.11) and Cs (0.07). Analysis of the product composition after 7.5 h revealed two trends (Figure 7d). First, there was a large increase in CO production at the expense of FA when switching from Na to K, Rb and Cs.
Second, increased production of CH₄ was observed with increasing alkali metal cation size. This was also reflected in the ratio of water to product generated, which was the largest for Cs–SiO₂-SL (63), more than four times higher compared to Na–SiO₂ (15).

Considering that the deposition of Na on SiO₂ yielded the best performance among the various alkali metals, the grafting procedure was repeated using various NaOH concentrations in methanol in an attempt to optimize the performance of Na–SiO₂ (Figure 8). Overall, the conversion of methanol followed the order: Na–SiO₂-0.15 M > Na–SiO₂-0.05 M > Na–SiO₂. The reverse sequence was obtained for the selectivity towards FA. Overall, all three catalysts resulted in a very similar yield of FA, which demonstrates that the optimization potential of the catalyst with respect to metal loading was limited. The impact of the change of solvent during grafting on the catalytic performance was also assessed by substituting methanol with isopropanol. The use of isopropanol resulted in a much less stable catalyst, as Na–SiO₂-IPA underwent rapid deactivation to lower methanol conversion level compared to the other catalysts. Moreover, during the first 3 h with this catalyst, the methanol conversion was above 60% and FA selectivity was below 0.25, confirming that high metal loading preferentially leads to complete methanol dehydrogenation to CO, especially during the transition phase.

With increasing reaction time, all samples suffered from a gradual decline in FA concentrations. Catalyst deactivation was frequently reported for the catalytic dehydrogenation of methanol, and was attributed to catalyst coking or evaporation of the active phase.[23] Depending on the cause of deactivation, the regeneration of the catalyst might be possible: evaporation of the active phase is an irreversible deactivation process while surface coke is removable by oxidative treatments. Considering that coke was deposited, which was indicated by a change of color of the powders from white to black after each run, catalyst regeneration by oxidative treatment was investigated using Na–SiO₂ (Figure 9).

During run 1, the FA yield was reduced from a maximum of 0.26 to 0.13 after 45 h, due to simultaneous reduction in FA selectivity and methanol conversion (Figure 9a). The loss in selectivity to FA was the result of an increase in CH₄ production at the expense of FA. Temperature-programmed oxidation (TPO) was performed to regenerate the catalyst activity, according to the protocol described in section 2.3 (Figure 9d and e). Regeneration by exposure to O₂ at high temperatures led to the release of CO₂ and CO, probably due to the removal of potential surface carbon deposits, as well as water. Similar results were obtained during the two oxidative treatments with the CO₂ peak observed at 575°C.

After the oxidative treatments, the catalyst activity changed at the beginning of the reaction with larger methanol conversion and lower selectivity compared to the initial run, which was accompanied by higher CO emission (Figure 9b and c). The time necessary to reach the maximum FA selectivity increased from 1 h to 10 h. It is likely that the exposure to O₂ at high temperatures changed the silica surface properties, which increased its activity for complete methanol dehydrogenation. However, the catalyst performance after the transition periods were similar during run 2 and 3 compared to run 1. The maximum FA yields reached during run 2 and 3 were slightly superior to the maximum yield obtained during run 1, but the reason for this increase is not clear. Overall, the catalytic activity of Na–SiO₂ could be regenerated by oxidative treatments and its deactivation is linked to surface coking, which was confirmed by TPO.

Our results confirm previous studies on methanol dehydrogenation over alkali-metal based catalysts, in which deactivation of the catalysts due to coking was reported.[23,39,40] The best FA

![Figure 8. Performance of the Na–SiO₂ catalysts grafted with various concentrations of NaOH and with isopropanol (IPA) (a) methanol conversion X_{MeOH}, (b) selectivity to FA S_{FA}, (c) FA yield Y_{FA}, and (d) product stream composition after 21 h on stream (indicated by a dashed line).](image-url)
yields of 20–30% obtained with sodium-grafted silica catalysts were still much lower compared to the yields of up to 70% reported by Ruf et al. for sodium metal vapor as catalyst in the reaction feed.\textsuperscript{[41]} By using a four component Ag-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-ZnO catalyst, Ren et al. have even claimed a FA yield of 86.1%.\textsuperscript{[42]} However, sodium-grafted silica catalysts showed better catalytic activity compared to Na-ZSM-5, which demonstrated comparable FA selectivity (69.9%) at reduced methanol conversion (5.7%).\textsuperscript{[23]}

3.3. Structure-activity relationship

Grafting of alkali metals on amorphous silica radically changed the activity of the initial material for the catalytic dehydrogenation of methanol. Various catalysts were synthesized using different alkali hydroxide salts or by changing the salt concentration during the grafting procedure. In order to understand how the structure of these catalysts affected their activity, several aspects must be discussed. First, the structure and chemistry of silica is briefly described. Then, the chemistry of alkali metals and their interaction with silica are outlined. Finally, the active sites for methanol dehydrogenation and a potential reaction mechanism are explored.

Amorphous silica is composed of tetrahedral SiO\textsubscript{4} units, yielding a complex surface made of rings, which comprise between six and twelve members (Scheme 2a).\textsuperscript{[43]} The silica surface also displays various types of hydroxyl groups, namely isolated, vicinal and germinal silanols (Scheme 2b). Their concentrations vary depending on the conditions: higher temperatures lead to dehydroxylation of the surface. Vicinal hydroxyl groups condense above 150°C, and at temperatures around 700°C, the silica surface becomes mainly decorated with isolated silanols. Above 700°C, the silica also restructures with a simultaneous loss of specific surface area and the formation of very reactive siloxane bridges such as the four-member ring. Considering the silica surface at a temperature of 650°C, an oxygen atom in silica can essentially exist in an isolated silanol (Si–OH) or in a siloxane group (Si–O–Si).\textsuperscript{[43]}

Due to the heterogeneity of the surface of amorphous silica, various sites can be formed by grafting of alkali metals. The cations are considered to be directly coordinated with the silanolate generated by deprotonation during the grafting procedure. However, it is likely that various cation adsorption structures exist on the surface after grafting. It was reported that adsorption of Na on silica following a treatment with NaOH resulted in Na\textsuperscript{+} ions forming monodentate, bidentate and tridentate configurations, by coordination with silanolate,
siloxane and hydroxyl groups, respectively. Likewise, the structure of the cationic sites in alkali metal-grafted USY zeolites was found to involve coordination with adjacent siloxane and silanol groups.

Assuming a successful grafting on the surface of silica by the method of Keller et al., Scheme 3 illustrates how the metal-oxygen bond and the silica framework are influenced by the coordination with an alkali metal. The chemistry of alkali metals is determined by their size and electronegativity. First, the Lewis basic character of the framework oxygen atoms augments with an increasing ionic character of the M–O bond, which changes strongly by substituting H with an alkali metal (Scheme 3a). The presence of an electropositive cation provokes an electron density shift on the surface of silica and

Scheme 2. Silica surface composed of (a) various cycle sizes of silanol bridges and (b) silanol groups.

Scheme 3. Influence of the alkali metal cation on the M–O bond and the silica lattice by change in (a) the electronegativity, (b) the cation size, and (c) the electron density shift.
increases the basicity of the adjacent oxygen bridge (Scheme 3c). The ionic character of the bond does not change greatly depending on the alkali metal: as the atomic weight increases, the bond polarity increases only slightly.

The change in electronegativity moving down the group 1 elements is relatively small compared to the change in charge density. Indeed, the metal cation size varies greatly moving down the group 1 elements of the periodic table (Scheme 3b): Cs$^+$ radius of 1.63 Å is more than twice the size of the radius of Li$^+$ (0.60 Å).\[^{[46]}\] The cation charge density varies proportionally to this change in size and the elements can thus be classified into two groups: high (Li, Na) and low (K, Rb, Cs) charge density cations.\[^{[35]}\] As observed during methanol-TPD, the electrostatic interaction of methanol with the alkali metals is strongly influenced by their charge density. The alkali metal ion can coordinate with the lone electron pair of methanol and this interaction is stronger for small ions due to their larger charge density. Generation of FA or CO during methanol-TPD was not affected by the nature of the ion. Therefore, it is more likely that FA and CO formation are the result of methanol bounding to siloxane bridges adjacent to silanolates accommodating the alkali metal.

Based on our experimental results, we can suggest two reaction mechanisms that could occur on the surface of the alkali metal-grafted silica. As previously reported, the first one considers that the dehydrogenation occurs on the siloxane bridge and that the alkali metal acts as the promoter (Scheme 4a).\[^{[37,47]}\] As the electropositive alkali metal shifts the electron density closer to the adjacent oxygen, its basicity increases. The oxygen is then more likely to interact with methanol by hydrogen abstraction from the hydroxyl group. Methanol adsorption results in the opening of the oxygen bridge with the generation of a methoxy and a hydroxyl group. Then, a hydrogen from the methoxy group combines with the adsorbed H to liberate H$_2$ as well as FA.

The second reaction mechanism assumes that the alkali metal cation is the active site (Scheme 4b). It was reported that methanol was converted to FA on alkali metal cations that are responsible for the alkylation of toluene on alkali metal-exchange zeolite Y.\[^{[48]}\] Methanol interacts with the alkali metal cation via the lone electron pair of the oxygen and its adsorption results in the elongation of its hydroxyl bond. Two intermediates can be formed depending on whether the first hydrogen is cleaved from the hydroxyl (i) or the methyl group (ii). Attempts to identify an intermediate have not yet been successful.\[^{[46]}\] Overall, FA is produced following a two-step process, which could involve a carbocation: abstraction of the first hydrogen and recombination with the second to form H$_2$. FA then interacts with the metal cation via its carbonyl group before desorbing.

The results of the catalysts characterization and the catalytic tests can provide additional insights into the reaction mechanism. Two parameters mainly influenced the activity of the catalysts during methanol catalytic dehydrogenation: the nature of the alkali metal and its concentration on the silica surface. First, a higher concentration of alkali metal on the silica surface resulted in a lower selectivity towards FA. When the surface exhibited a higher concentration of alkali metals such as K, Rb, or Cs (M–SiO$_2$ series), a large fraction of methanol was converted to CO. Likewise, a lower FA selectivity was observed when Na was grafted with the highest NaOH concentration (Na–SiO$_2$–0.015) or with isopropanol (Na–SiO$_2$–IPA). We can conclude from all our results that the loss in selectivity towards...

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**Scheme 4.** Suggested reaction mechanisms for the catalytic dehydrogenation of methanol involving (a) the siloxane bridge or (b) the alkali metal cation.

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FA with an increasing metal concentration on the silica surface occurs independently of the nature of the alkali metal.

The second parameter that severely influenced the performance of the catalysts was the nature of the alkali metal. For a range of M:Si molar ratios between 0.0087 and 0.0281 (Li–SiO$_2$, Na–SiO$_2$ and the M–SiO$_2$-SL series), a large difference in FA selectivity was observed between high and low charge density cations and it followed the trend: Li > Na > K > Rb > Cs. These results can be compared to a study from Kang et al., who investigated the adsorption of methanol on alkali-cation-exchanged zeolite using DFT (excluding Li$^+$). Although it is an amorphous network of silicon tetrahedra, silica can be compared to a zeolite, when the different crystallinity and source of negative charge are considered. Their study demonstrated that the energy of adsorption of FA via interaction of the carbonyl bond of FA with the alkali metal was increasing for larger alkali metals.

Similarities can be seen between this DFT study and the results from our catalytic tests. The selectivity towards FA decreased with an increasing atomic number of the alkali metals (Table S1). As FA is unstable at 650 °C, it is clear that it must desorb rapidly from the surface of the catalyst to prevent further decomposition to CO and H$_2$. Therefore, it is plausible to assume that the decrease in FA selectivity observed in the catalytic tests is related to the higher adsorption energy of FA on larger alkali metals. As a consequence, FA remains longer on the surface and has a higher probability of being completely dehydrogenated to CO. However, further research is needed to decide which of the two proposed reaction mechanisms is better suited to describe the surface chemistry (Scheme 4). In-situ spectroscopy and DFT analysis could provide additional insights on the possible intermediates that are formed on the catalysts surface.

The application of the simple method of alkali metal grafting on silica and its use for catalytic methanol dehydrogenation has revealed new and interesting perspectives. In our study, we were able to identify a tradeoff between alkali metal loading and surface amorphization. New strategies to further optimize catalyst loading should therefore be considered in future work to improve catalyst performance. For example, the effect of pretreatments of the silica prior to grafting should be investigated to understand the influence of the silica surface and the different grafting sites on the catalytic activity. Additional analysis could help to better understand the aging of the catalysts during and after the reaction. The structure of the support could be another aspect to be optimized in order to minimize the formation of byproducts and the coking of the catalyst. Based on the highest selectivity to FA found over the lithium sample, the synthesis and grafting method should be fine-tuned to increase the Li loading on the silica surface.

4. Conclusions

With this work, we have extended the use of alkali metals for the catalytic dehydrogenation of methanol to formaldehyde by anchoring them on fumed silica as stable support material. To this end, grafting with alkali hydroxide salts in alcohol was used for the first time to prepare catalysts for this reaction. The basicity of the salt was a crucial parameter: a higher metal loading was achieved using hydroxide salts with larger alkali metal cations. Varying the salt concentration and the solvent also affected the catalyst loading. Overall, a trade-off between metal loading and surface amorphization was observed, demonstrating the limit of alkali metal deposition on the silica surface using this method. Sodium grafting on fumed silica resulted in a moderate metal loading, which yielded the best combination of high FA selectivity and moderate methanol conversion.

The resulting catalysts displayed an increased activity for the catalytic dehydrogenation of methanol. Two active sites were identified: the metal cation and the siloxane bridge adjacent to it. The varying electron density of the supported alkali metal cation severely affected the FA selectivity, which followed the trend: Li > Na > K > Rb > Cs. A large drop was observed between cations of high (Li, Na) and low charge density (K, Rb, Cs), which was triggered by the increasing adsorption energy of FA on a metal cation of a decreasing charge density. Considering these results, two reaction mechanisms for methanol dehydrogenation were proposed where the alkali metal is either the active species, or acts as promoter to the adjacent siloxane bridge.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] G. Reuss, W. Disteldorf, A. O. Garner, A. Hilt, Ullmann’s Encycl. Ind. Chem. 2012, 444–487.
[2] M. Maiwald, H. H. Fischer, M. Ott, R. Peschla, C. Kuhnert, C. G. Kreiter, G. Maurer, H. Hasse, Ind. Eng. Chem. Res. 2003, 42, 259–266.
[3] A. M. Bahmanpour, A. Hoadley, A. Tankalsale, Rev. Chem. Eng. 2014, 30, 583–604.
[4] E. L. Aneke, J. J. J. Ridder, P. J. Berg, J. R. Netherlands Chem. Soc. 1981, 100, 236–240.
[5] S. Su, P. Zaza, A. Renken, Chem. Eng. Technol. 1994, 17, 34–40.
[6] G. I. N. Waterhouse, G. A. Bowmaker, J. B. Metson, Appl. Catal. A 2004, 265, 85–101.
[7] P. Zaza, H. Randall, R. Doepper, A. Renken, Catal. Today 1994, 20, 325–334.
[8] S. Su, M. R. Prairie, A. Renken, Appl. Catal. A 1992, 91, 131–142.
