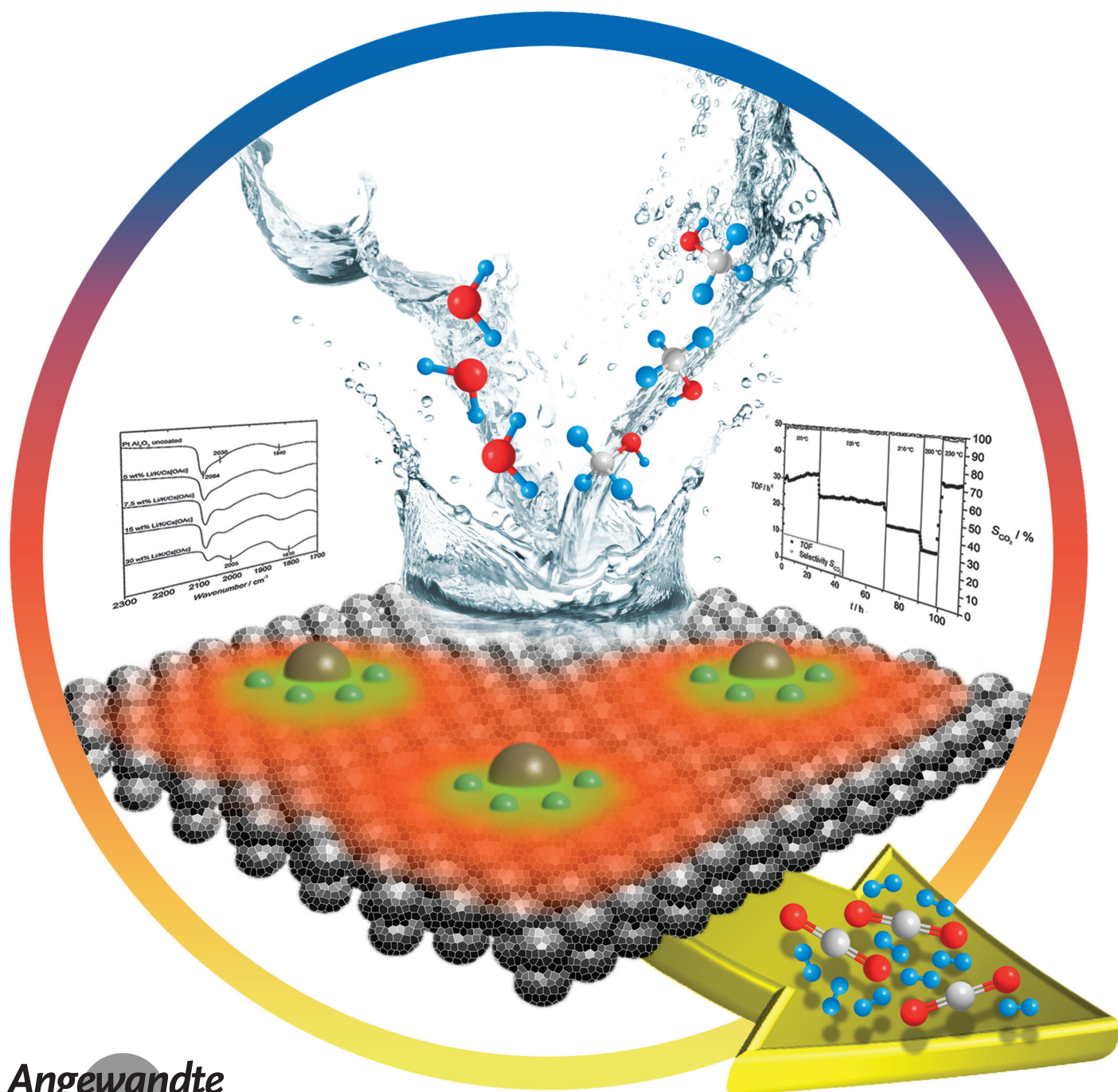


Enhanced Activity and Selectivity in Catalytic Methanol Steam Reforming by Basic Alkali Metal Salt Coatings**

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Steam reforming is the method of choice if hydrogen has to be produced from methanol in high yields.^[1] Under ideal conditions, the reaction converts methanol and water into carbon dioxide and three moles of hydrogen in a moderately endothermic transformation, as shown in Equation (1).



Currently, steam reforming of methanol is receiving much attention in the context of methanol-based energy-storage systems.^[2] Methanol is considered as a promising candidate for hydrogen storage to utilize regenerative excess energies. To complete the storage cycle, more efficient catalyst systems for MeOH steam reforming are of great technical interest. Such decentralized hydrogen production from MeOH would greatly benefit from high catalyst selectivity towards H₂ and CO₂ at the lowest possible temperature. Formation of CO has to be avoided as much as possible, because CO acts as a strong poison for almost all fuel cell catalysts.^[3] Low temperature activity is highly desirable to leverage heat integration potentials between the endothermic steam reforming and the exothermic fuel cell operation. Currently, the reported limit for high temperature PEM (proton exchange membrane) fuel cell systems is 180 °C.^[4] This is a temperature level too low for operating the MeOH steam reforming reaction with high hydrogen yields.

Two different classes of heterogeneous catalysts dominate research and industrial practice of MeOH steam reforming: Pd or Pt on different types of supports and Cu/ZnO systems.^[1–5] The commercial Cu/ZnO systems are indeed very active and selective but they require lengthy activation

procedures. Typically, the catalyst is in contact with a diluted stream of hydrogen for several hours. Such catalyst preformation is inappropriate for most fluctuating hydrogen production scenarios. In addition, Cu based catalysts are highly pyrophoric in their activated state, a fact that complicates the practical handling of these materials in dynamic on–off cycles.

Because of these unfavorable characteristics of the Cu/ZnO systems we focused our research on optimization of supported Pt catalysts for MeOH steam reforming. Herein, we report that Pt on alumina catalysts exhibit an exceedingly enhanced activity and selectivity after surface modification with a thin-film coating of hygroscopic and basic inorganic salts.

Initially, our idea was to modify the Pt on alumina system by a molten salt coating to benefit from the known low hydrogen solubility of these liquid salts for manipulating the hydrogen release kinetics of the system.^[6] Chemical modification of heterogeneous catalyst contacts by liquid salt films is not new and is referred to as solid catalyst with ionic liquid layer (SCILL) in literature.^[7] SCILL catalysts take advantage of specific physico-chemical properties of the ionic-liquid (IL) coating (e.g. differential solubility effects)^[6] but also benefit from distinct chemical interactions between the liquid salt and the active surface sites. Owing to the extremely low vapor pressure of the IL, the IL film resides on the catalyst surface under the conditions of continuous gas-phase reactions. Enhanced selectivities have been demonstrated for SCILL systems, for example, in hydrogenation catalysis.^[8] Recently, the microscopic origin of the observed selectivity effects for SCILL systems has been explained by a series of surface-science experiments.^[9]

From previous work, we knew that ionic liquids carrying organic, heterocyclic cations (e.g. imidazolium ions) would not withstand the reaction conditions applied in MeOH steam reforming (temperatures up to 230 °C; vapor atmosphere). Some of us have reported recently that slow imidazolium hydrolysis takes place under these conditions, liberating coordinating amines.^[10] Consequently, we selected for this work the inorganic molten salt mixture Li/K/Cs acetate (molar ratio = 0.2/0.275/0.525)^[11] for modifying the surface of the Pt (5 wt %) on alumina catalyst. The applied salt mixture has a glass transition point at 33 °C and a melting point in the dry state of 119 °C.^[12] At a typical reaction temperature of 200 °C, its density in the dry state is 2.06 g cm⁻³ and its viscosity is 39 mPas. This mixture is highly hygroscopic and the addition of water sharply decreases the melting point, viscosity, and density. The molten-salt-coated Pt on alumina catalyst was obtained by applying a defined amount of salt to the heterogeneous catalyst in water, followed by solvent removal and drying under vacuum. The amount of mixture was calculated to adjust a certain mass loading, with *w* being the mass of salt divided by the mass of the neat catalyst.

All MeOH steam-reforming experiments were carried out in a continuous fixed bed reactor set up (see Supporting Information for details) by bringing the catalyst in contact with a gaseous stream of MeOH and water. Figure 1 and 2 show the catalytic performances of the uncoated Pt on alumina catalyst (Figure 1) and the respective salt-modified

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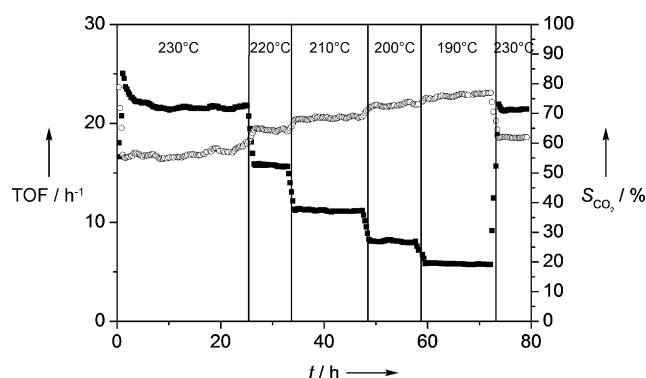


Figure 1. Continuous steam reforming of methanol using an uncoated Pt/alumina catalyst (■ = TOF; ○ = S_{CO_2}). Experimental conditions: $T = 230\text{--}190^\circ\text{C}$ (see vertical lines); $p_{\text{tot}} = 5$ bar; $p_{\text{MeOH}} = p_{\text{H}_2\text{O}} = 0.5$ bar; $m_{\text{cat}} = 401.4$ mg; $\tau = 10$ s.

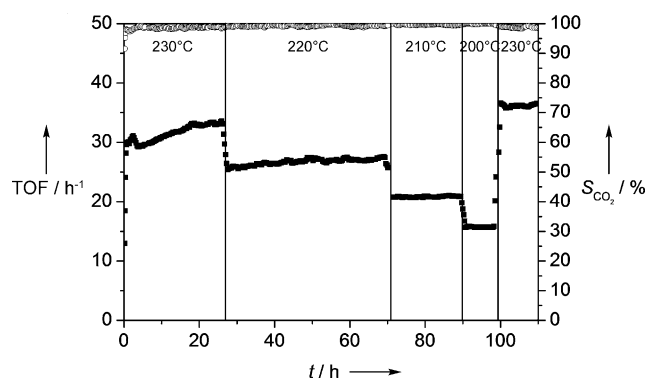


Figure 2. Continuous steam reforming of methanol using a Li/K/Cs[OAc] coated Pt/alumina catalyst, $w = 30$ wt% (■ = TOF; ○ = S_{CO_2}). Experimental conditions: $T = 230\text{--}200^\circ\text{C}$; $p_{\text{tot}} = 5$ bar; $p_{\text{MeOH}} = p_{\text{H}_2\text{O}} = 0.5$ bar; $m_{\text{cat}} = 521.8$ mg; $\tau = 10$ s.

catalyst ($w = 30$ wt%; Figure 2) for comparison. Both experiments used the same molar amount of Pt ($n_{\text{Pt}} = 1 \times 10^{-4}$ mol) and very similar reaction conditions (residence time $\tau \approx 10$ s, temperature range $190\text{--}230^\circ\text{C}$ in defined steps).

Remarkably, the molten-salt-coated catalyst exhibited a strongly enhanced CO_2 selectivity (99% CO_2 selectivity at 230°C with coating compared to 62% without coating) and a significantly higher catalytic activity (turn over frequency (TOF) = 36 h^{-1} at 230°C with coating compared to 22 h^{-1} without coating; all TOF values were calculated with respect to the total Pt content of the catalyst). For the catalyst with salt modification, an activation energy of $55 \pm 2\text{ kJ mol}^{-1}$ was determined, compared to $64 \pm 2\text{ kJ mol}^{-1}$ for the uncoated catalyst.

A variation of the salt loading w in subsequent experiments (5–30 wt%, see Figure 3) showed a remarkable dependency of the catalyst performance on the level of molten-salt loading (Figure 3 and 4). For loadings above 7.5 wt%, a step change in activity and selectivity was observed, while loadings of only 5 wt% caused even a slight deactivation as compared to the unmodified catalyst. Reasons for this behavior include the fact that the molten salt coating is very hygroscopic and basic. Thus, the molten-salt layer increases the availability of water at the active sites, while the very low solubility of H_2 in the salt leads to effective H_2 removal from the active surface. The concentration of

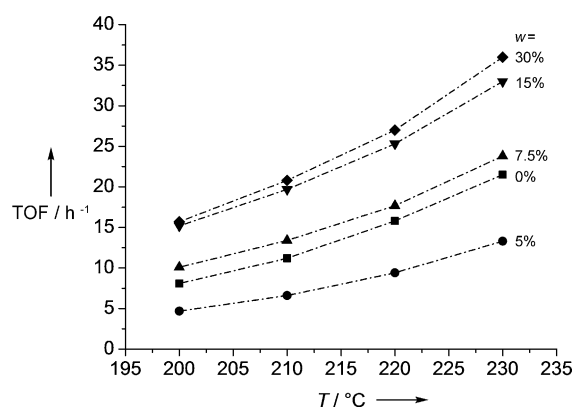


Figure 3. Turn over frequency versus temperature for different Li/K/Cs acetate salt loadings (w) in continuous methanol steam reforming catalysis: $T = 200\text{--}230^\circ\text{C}$; $p_{\text{tot}} = 5$ bar; $p_{\text{MeOH}} = p_{\text{H}_2\text{O}} = 0.5$ bar; $n_{\text{Pt}} = 1 \times 10^{-4}$ mol; $\tau = 10$ s.

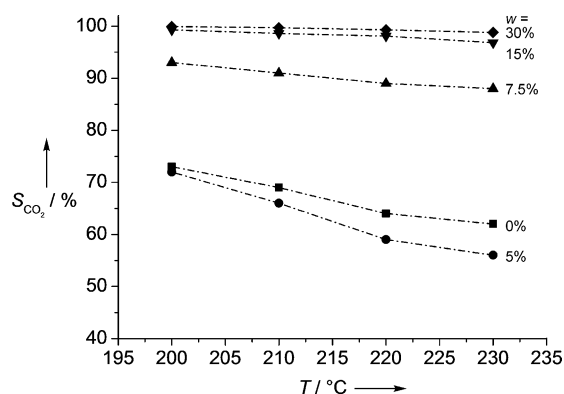


Figure 4. CO_2 selectivity versus temperature for different Li/K/Cs acetate salt loadings (w) in continuous methanol steam reforming catalysis: $T = 200\text{--}230^\circ\text{C}$; $p_{\text{tot}} = 5$ bar; $p_{\text{MeOH}} = p_{\text{H}_2\text{O}} = 0.5$ bar; $n_{\text{Pt}} = 1 \times 10^{-4}$ mol; $\tau = 10$ s.

hydroxide ions is known to play an important role in the catalytic conversion of CO and water into CO_2 and hydrogen (water–gas shift reaction, WGSR).^[13] The basic acetate coating obviously enhances the rate of this step, leading to a drastic shift in selectivity.

We next investigated whether the presence of alkali ions in the molten salt, in addition to its hygroscopic and basic nature, was also relevant for the enhanced performance of the catalyst. Promotion of catalytic activity by alkali ions is known in the literature under the term “alkali doping” and is of highest technical relevance to the performance. The preparation of industrial catalysts for ammonia or methanol synthesis, hydrogenation or dehydrogenation reactions, as well as sulphuric acid production involve the use of alkali-containing compounds.^[14] In the case of the WGSR and MeOH steam reforming, it has been reported that lithium- or sodium-doped Pt/ceria catalysts are more active than the respective unmodified catalysts. As demonstrated in the literature by diffuse reflectance infrared Fourier transform (DRIFT) investigations, the main reason for these enhanced activities is a weakening of the C–H bonds of the formate intermediates by the alkali dopant leading to an accelerated dehydrogenation of the reaction intermediates.^[15] In the case

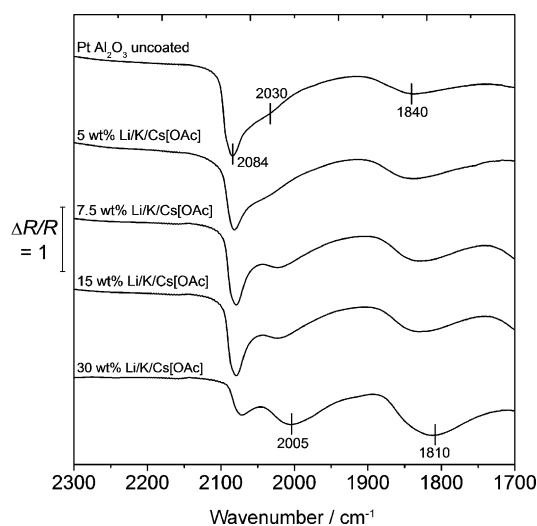


Figure 5. CO region of the DRIFTS spectra for different salt loadings (w , increasing from top to bottom).

of the WGS with Pt on Al_2O_3 modified by sodium or potassium hydroxide, it has been proposed that the active Pt species becomes partly oxidized through the respective alkali oxides leading to an enhanced CO adsorption and water activation.^[16] For H_2 production through formic acid decomposition, it has been reported that the reaction rate of a Pd/C catalyst could be enhanced by one to two orders of magnitude through surface modification with potassium.^[17]

To check such influences for our molten salt coated systems, IR spectroscopic investigations were carried out with a DRIFTS spectrometer. Figure 5 shows the CO region for loadings $w = 0$ –30 wt %. Starting with the spectra of the uncoated surface, the largest absorption is visible at 2084 cm^{-1} with a shoulder at 2030 cm^{-1} and a less intense feature at 1840 cm^{-1} . The intensity of the band at 2084 cm^{-1} remains mostly unchanged up to 15 wt % but is only half as intense at 30 wt %. The band at 2030 cm^{-1} continuously shifts to lower wavenumbers and distinguishes itself from the higher frequency band at $w = 7.5$ wt %. The feature at 1840 cm^{-1} shifts similarly and gains intensity with increased loading. The evolution of the bands is such that the relative intensities on the spectra acquired for $w = 30$ wt % loading are completely different from the rest of the series, with the band at 2084 cm^{-1} shifting to the less intense one and the bands at 2030 cm^{-1} and 1840 cm^{-1} dominating the spectra.

CO on Pt particles is a well-studied system and we can interpret our spectra based on the literature. The band at 2084 cm^{-1} is known to correspond to on-top CO at terraces, the band at 2030 cm^{-1} to on-top CO at particle edges, and the less intense band at 1840 cm^{-1} to CO bridged on terraces.^[18] Notably, the intensities measured do not reflect the abundance of CO on the different sites because of the dipole coupling and intensity transfers occurring on the metallic surfaces.^[19] Surface science studies on alkali doping provide an interpretation of the spectral changes observed herein.^[20] Indeed, the loss of intensity of the 2084 cm^{-1} band and the shift of the other two bands suggest that the alkali metal displaces on-top CO at terraces and particle edges to the bridged sites on the terraces. Other effects proposed are

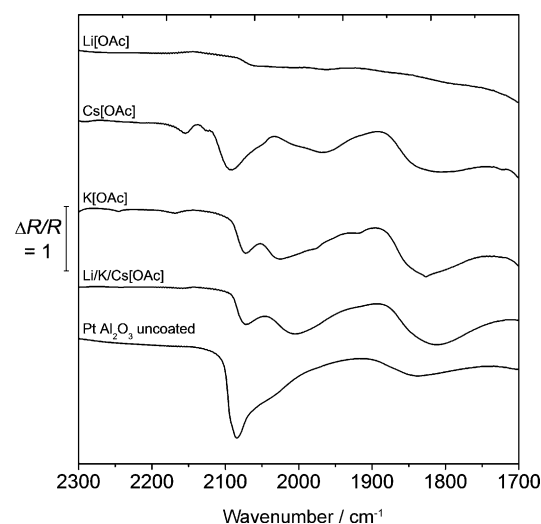


Figure 6. CO region of the DRIFTS spectra for different alkali acetates: lithium, cesium, potassium acetate, and the mixture of the three acetates, compared to the uncoated Pt catalyst.

short-range interactions between the dopant and CO and electron transfer from the alkali to the antibonding 2π orbitals of CO by way of the Pt d-bands.^[20]

Figure 6 shows spectra with $w = 30$ wt % loading acquired with the mixture used in the catalytic tests compared to the separated components at a comparable loading and a clean surface. Pure Li[OAc] and pure Cs[OAc] have remarkably different spectroscopic signatures compared to the mixture. In contrast, the K[OAc] spectrum exhibits clear similarities with the spectra of the salt mixture, showing that—within the mixed molten salts—potassium has the strongest affinity for the surface. The effect of alkali doping originates from an electron transfer from the alkali metal to the substrate, resulting in stronger bonding of the adsorbed gas. Potassium was reported to have the strongest influence on Pt(111).^[20] At the surface, the salt mixture and pure K[OAc] have very similar effects on the spectra compared to elemental potassium.^[20]

We next tried to verify the influence of K[OAc] in the applied salt mixture on the MeOH steam reforming catalysis. Fortunately, the melting points of the applied salts were not a limiting factor for the specific case of MeOH steam reforming, because the presence of water in the catalyst pores liquefies any hygroscopic salt coating. Therefore, it was possible to test the coating effect of the three alkali acetates separately (the salt coating was 30 wt % for each). In excellent agreement with our spectroscopic results, we found that the catalyst coated with potassium acetate showed the highest increase in activity and selectivity compared to the neat Pt on alumina contact (all catalytic results are shown in the Supporting Information). Note that the system coated with K[OAc] showed stable catalytic performance down to 200°C , despite the melting point of the salt being as high as 292°C , again reflecting the extremely hygroscopic nature of this salt. The same catalyst system showed stable activity and selectivity over 500 h on-stream indicating that the beneficial effect of the salt coating is not lost over time by leaching or salt decomposition effects (see Supporting Information). In line

with our hypothesis that a hygroscopic, basic, and K^+ containing salt would cause the strongest enhancement in activity and selectivity, we also tested coatings of equimolar amounts of KOH ($w = 17.15 \text{ wt } \%$) and $K[\text{HCO}_3]$ ($w = 30.6 \text{ wt } \%$) on the same Pt on alumina contact under otherwise identical conditions. As expected, we also found drastically enhanced activity and selectivity (at $T = 230^\circ\text{C}$: $\text{TOF}_{\text{KOH}} = 50 \text{ h}^{-1}$, $S_{\text{CO}_2, \text{KOH}} = 99\%$ and $\text{TOF}_{\text{K}[\text{HCO}_3]} = 41 \text{ h}^{-1}$, $S_{\text{CO}_2, \text{K}[\text{HCO}_3]} = 99.5\%$; for details see the Supporting Information) compared to the uncoated Pt on alumina contact (at $T = 230^\circ\text{C}$: $\text{TOF}_{\text{uncoated}} = 22 \text{ h}^{-1}$, $S_{\text{CO}_2, \text{uncoated}} = 62\%$). A comparable experiment with a $\text{K}[\text{NTf}_2]$ coated catalyst revealed very low catalytic activity and selectivity ($\text{TOF}_{\text{K}[\text{NTf}_2]} = 2 \text{ h}^{-1}$, $S_{\text{K}[\text{NTf}_2]} < 15\%$), demonstrating that the interplay of alkali doping, salt hygroscopicity, and salt basicity is essential for the observed catalyst modification effects.

In conclusion, we have demonstrated a synthetically straight-forward, highly effective way to drastically enhance the activity and selectivity of heterogeneous Pt contacts in the methanol steam reforming reaction. According to our spectroscopic findings, alkali doping by potassium species certainly plays an important role but additional contributions from the hygroscopicity and basicity of the salt were also found. We anticipate that the modification of classical heterogeneous catalysts by molten salt coatings can be used in the future as a rational and general approach to optimize heterogeneous catalysts through surface modification or co-adsorption effects. Further exploring the potential of this method should cause advances in molten-salt chemistry, surface science, catalyst preparation, and reaction engineering.

Experimental Section

Materials: Pt on aluminum oxide was purchased from Alfa Aesar (LOT: F02R004, Pt content = 4.86 wt %). $\text{Li}[\text{OAc}]$, $\text{K}[\text{OAc}]$, $\text{Cs}[\text{OAc}]$, $\text{K}[\text{HCO}_3]$ were received from Sigma Aldrich with a purity of 99.99%. KOH (Merck) was of 99.9% purity.

Synthesis of salt-modified catalysts: The calculated amount of Pt on support was immersed into a solution of the salt or salt mixture in water (typically 20 mL). After mixing for 30 min at 25°C the solvent was removed under vacuum.

Catalytic experiments: The catalyst performance in MeOH steam reforming was evaluated in a continuously operated gas-phase fixed-bed reactor similar to the one described elsewhere^[21] (details are found in the Supporting Information). An equimolar mixture of MeOH and water was evaporated and fed into the reactor. At the reactor outlet, unconverted MeOH and water were condensed and the product gas was analyzed by GC (Varian CP 4900). Catalyst activities are given as turn over frequencies (TOF), which is the total molar flow of carbon monoxide, carbon dioxide, and methane divided by the total molar amount of platinum in the reactor (typically $1 \times 10^{-4} \text{ mol}$). Selectivities S_{CO_2} are given as the CO_2 mole fraction in the outlet gas stream divided by the sum of the moles of CO_2 , CO, and CH_4 . The mass balance was closed by the quantification of the inert gas, nitrogen.

DRIFTS experiments: The catalyst characterization was performed in a Bruker Vertex 80v infrared spectrometer equipped with a Praying Mantis and a high temperature reaction chamber (HVC-DRP-4) from Harrick. An extension with all necessary feed-throughs was adjoined to the sample chamber of the spectrometer to allow for the evacuation of the optical path. Mass flows and pressures were regulated using Bronkhorst mass flow and pressure controllers. Prior to CO adsorption, the catalyst powder was heated under an Ar flow

(Linde, $> 99.9999\%$, $10 \text{ mL}_N \text{ min}^{-1}$, 1 bar) at 300°C for 30 min to desorb water and other contaminants. After exposure to CO (Linde, $> 99.997\%$, $10 \text{ mL}_N \text{ min}^{-1}$) at 25°C for 10 min, the reactor was purged thoroughly with Ar for 60 min until no CO gas-phase signal could be detected anymore. The IR spectra were recorded with a spectral resolution of 2 cm^{-1} , 1024 scans, and a scanning speed of 40 kHz. The reference spectrum was pristine alumina exposed to the same treatment.

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