

Promotion of heterogeneous catalysts

Abstract Supported metal-based heterogeneous catalysts are widely used in all areas of chemistry. The catalytic performance of metal catalysts can be improved by addition of small amounts of so-called promoters, which can be either metals or non-metallic elements. The promoters can modify the dispersion, morphology and intrinsic activity of the catalytically active phases. They may affect the catalyst texture and mechanical properties and even introduce new types of catalytically active species. Very often, the promoter distribution on the catalyst surface is considered to be uniform and immobile. Selective deposition and use of highly mobile promoters such as soldering metals, carbon species and iodine provide unique opportunities for design of highly efficient and sustainable heterogeneous catalysts and for performing catalytic reactions in a different way. The elaborated strategy significantly improves catalyst activity, selectivity to the target products, and stability. Several examples of this strategy are given in this article for the reactions of Fischer-Tropsch synthesis, amination and etherification.

Keywords Heterogeneous catalysis, metal nanoparticles, promoters, selective deposition, activity, selectivity, stability.

Résumé Promotion des catalyseurs hétérogènes

Les catalyseurs hétérogènes à base de métaux supportés sont largement utilisés dans tous les domaines de la chimie. Les performances catalytiques des catalyseurs métalliques sont susceptibles d'être améliorées en ajoutant de petites quantités de ce que l'on appelle des promoteurs, qui peuvent être des métaux ou des éléments non métalliques. Les promoteurs peuvent modifier la dispersion, la morphologie et l'activité intrinsèque des phases actives. Ils peuvent aussi influencer sur la texture et les propriétés mécaniques du catalyseur, et même introduire de nouveaux types d'espèces catalytiquement actives. Très souvent, la distribution du promoteur à la surface du catalyseur est considérée comme uniforme et immobile. Le dépôt sélectif et l'utilisation de promoteurs très mobiles tels que les métaux de soudure, les espèces de carbone et l'iode offrent des opportunités uniques pour la conception de catalyseurs hétérogènes hautement efficaces et durables. La stratégie élaborée améliore considérablement la sélectivité de l'activité vis-à-vis des produits cibles et la stabilité du catalyseur. Plusieurs exemples de cette stratégie sont présentés dans cet article pour les réactions de synthèse Fischer-Tropsch, l'amination et l'éthérification.

Mots-clés Catalyse hétérogène, nanoparticules métalliques, promoteurs, dépôt sélectif, activité, sélectivité, stabilité.

The key role of promoters

About 90% of chemical processes use catalysts, which results in the impact of catalysis on economic of about 30-40% of global gross domestic product (GDP). Most part of these catalysts are heterogeneous where the reaction takes place at the solid catalyst surface. Noble and transition metal-based catalysts have found numerous applications in the reactions of hydrogenation, dehydrogenation, oxidation, hydrocracking, etc. Although some industrial processes use pure bulk metal catalysts (Ni, Co Raney), the supported catalytic materials have significant advantages [1]. Deposition of small metal nanoparticles over the support (alumina (Al_2O_3), silica (SiO_2)) significantly increases the available metal surface area due to high metal dispersion. At the same time, accessibility of the catalyst surface to reagents is also improved with increase of the catalytic activity. However, small size metal nanoparticles contain different surface planes and unsaturated sites leading to side reactions decreasing the selectivity to the target product and may cause environmental problems. Catalyst deactivation is another important industrial problem [2]. Major deactivation mechanisms involve metal sintering and carbon deposition over metal sites during reaction. Modification of the properties of metal catalysts by promoters is a common way to enhance the efficiency of the catalysts in terms of activity, selectivity and stability. Promoters are chemical compounds, which are added in small amounts

(usually less than 1 wt.%) to the catalysts. The promoter is generally considered as an additive, which is inactive itself but can change the catalytic performance. In fact, the economic efficiency of most part of existing chemical processes depends on promoters. For example, epoxidation of ethylene to ethylene oxide as the main chemical intermediate (20 million metric tons per year (MMt/yr)) requires treatment of silver by chlorine. Ammonia is the largest volume chemical (145 MMt/yr) used for the synthesis of fertilizers. The Haber-Bosch process of ammonia synthesis from N_2 and H_2 would be impossible without promoting of iron-based catalyst by potassium.

The catalyst promoters are usually divided in two major classes: structural promoters, and electronic promoters. The structural promoters affect formation and stability of the catalysts and its active phase, while the electronic promoters modify the local electronic structure of active metals mostly by adding or withdrawing electron density. The electronic promoters also directly affect adsorption/desorption and elementary reaction steps. In addition, the promoter can also create new active sites, change the catalyst acid-base properties and metal-support interaction.

Different metallic (Na, K, Pt...) and non-metallic elements (S, Sn, C...) can be considered as promoters of metal catalysts. Alkali metals such as potassium and sodium, which are electropositive elements, are often used as promoters. For example, the presence of alkali promoters enhances the

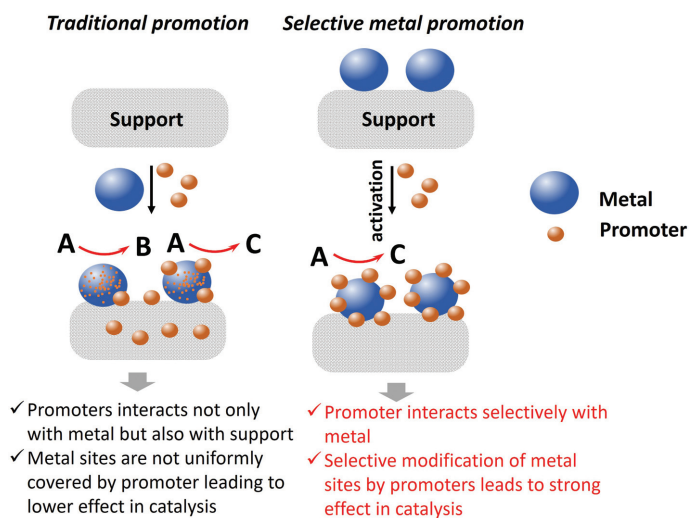


Figure 1 - Modification of metal catalysts by promoters for reaction A to C. Traditional promotion leads to broad distribution of promoter in comparison with selective modification.

catalytic activity in the reactions of CO and hydrocarbon oxidation, NO_x reduction, etc. [3]. At the same time, addition of tin and sulfur usually leads to catalyst partial deactivation, however with increase of the selectivity to specific products due to electronic or geometric effects.

The promoter can deactivate the catalyst itself due to decrease in the amount of active sites, however it could improve the selectivity or stability of the catalyst. The promoter is usually added to the catalyst during preparation simultaneously or consequently with a metal precursor (figure 1). The disadvantage of this route is that promoter can interact with catalyst in multiple ways: form mixed phase or alloy, modify surface of metal nanoparticles and interact with the support. Thus, the promoter has multiple effects on the metal, resulting in mixed promoted and non-promoted behaviors of the catalysts. During the catalyst activation and catalytic reaction, the promoter is usually considered as immobile, and is distributed between the catalytically active phase and support.

Alternatively, selective modification of metal nanoparticles by promoters, which directly interact with the surface of metal nanoparticles, leads to the new metal active sites surrounded by specific environment for more efficient catalysis.

Several conditions have to be satisfied in order to induce selective specific interaction between metal and promoter (figure 1):

- promoter should have strong affinity to the metal surface;
- promoter should be selectively deposited or migrate to the metal surface during catalyst synthesis, catalyst activation or reaction.

There are several examples in the literature which demonstrate selective interaction of promoter with surface metal sites leading to strong effect in catalytic performance. For example, modification of Pd by thiols resulted in modification of Pd surface for selective hydrogenation of internal alkynes to olefins [4]. The high catalytic selectivity and activity has been assigned to combined steric and electronic effects that inhibited the deeper hydrogenation of C=C bonds. Hereby, we would like to demonstrate our recent results relevant to the control of the catalytic performance of metal catalysts in different reactions using direct promotion by metallic and non-metallic promoters. In view of the broad diversity of chemical reactions for which it is desired to increase the catalytic performance of metal catalysts, it is

indeed unlikely that a single route can provide the desired promoting effect for chemical reactions as different as, for example, Fischer-Tropsch synthesis, amination and etherification reactions. Thus, our approach has been to develop not one, but several kinds of promoters, as different as metallic and non-metallic promoters, each kind of promoter being specifically designed for control of activity, selectivity and stability in a given kind of reaction.

In particular, we would like to demonstrate that promoters based on soldering metals, carbon species or halogens, using selective promoting strategy can modify the performance of metal-based catalysts in terms of activity, selectivity and stability. We will also show that the promoters can modify the reaction not only *via* electronic, structural or steric effects, but also by providing new sites for catalytic reactions.

Liquid metal promoters for Fischer-Tropsch synthesis over Fe and Co catalysts

Fischer-Tropsch (FT) synthesis produces hydrocarbons and oxygenates from syngas (H₂/CO mixtures), which might be generated from biomass, coal and natural gas [5]. Low temperature FT synthesis, which occurs at 220-240 °C, 20 bar and H₂/CO molar ratio of 2 over cobalt-based catalysts, is used nowadays for the production of renewable fuels. High temperature FT synthesis proceeds at the temperature higher than 300 °C usually over iron-based catalysts makes light hydrocarbons and olefins. Light C₂-C₄ olefins are basic feedstocks in chemical industry for the production of polymers, chemical intermediates and solvents.

A study of the effect of numerous promoters by high-throughput screening of Fe catalysts led us to the low melting point metals such as Bi and Pb [6-7]. These metals are typically used as solders in plumbing, electronics, metalwork, and other applications. STEM-EDX analysis of the metal distribution before and after catalyst activation or reaction demonstrates that Bi or Pb migrates to Fe due to higher affinity to the metal phase than support and high mobility of promoters (figure 2). The core-shell structures with Bi and Pb on the surface of Fe phase were uncovered in the catalysts by STEM-EDX.

We have discovered that the promotion of iron catalysts with Bi and Pb leads to an exceptional increase in FT reaction rate (up to 10 times) and higher selectivity to light olefins (up to 60%) (figure 3). In addition, FT synthesis can be conducted under very mild conditions and even at atmospheric pressure. Conventional non-promoted iron catalysts exhibit almost zero activity at atmospheric pressure under the same conditions.

These promoting metals are crucial for the enhancement of the selectivity and activity due to several factors. First, these metals have melting points at temperatures lower (T_{Pb} = 327 °C; T_{Bi} = 271 °C) than the temperature of FT reactions (~350 °C). This leads to a pseudo-liquid state of the promoters under the reaction conditions, their intensive migration, and close contact between Fe and the promoters. The second important feature of these metals is several oxidation states and easy redox cycles between metal and oxide. Our results using XPS and *in situ* EXAFS suggest that liquid metal promoters may facilitate carbon monoxide dissociation on the surface of the Fe catalyst by O scavenging with Bi and Pb (figure 4). This results in significant increase in the catalytic activity of the catalysts to light olefins.

Another important effect, which has been observed during FT synthesis in the presence of Bi- and Pb-promoted catalysts,

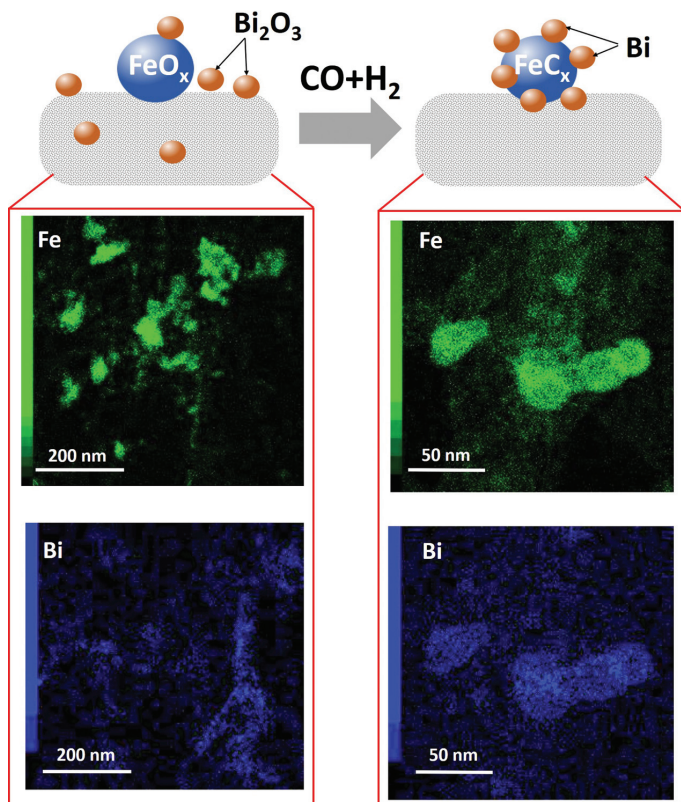


Figure 2 - TEM-EDX images of Fe/CNT catalyst promoted by Bi for freshly prepared catalysts and after syngas treatment. Before syngas treatment, localization of Bi and Fe is different, and after syngas treatment, Bi is on the surface of Fe [6-7].

is higher stability [8]. The effect has been observed both for the high and low temperature FT synthesis (figure 3). The presence of the promoter at the interface of metal nanoparticles and support seems to slow down both carbon deposition and metal sintering. The effect has been ascribed to the protective shell of pseudo-liquid metal, which is

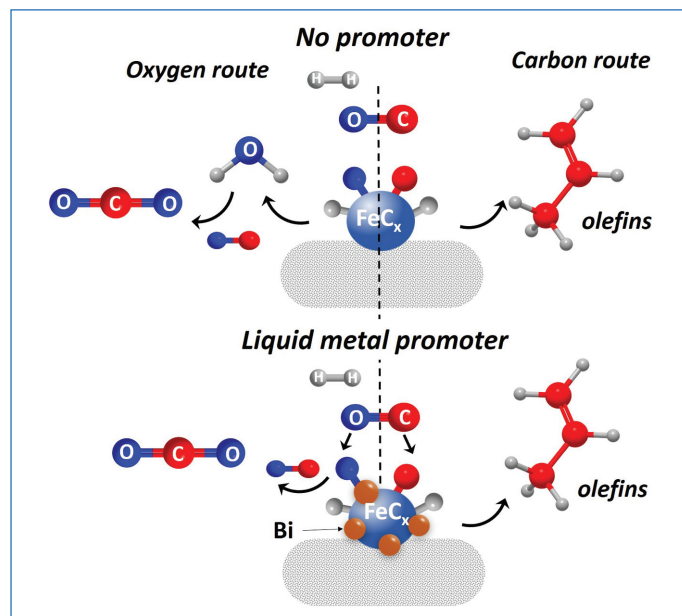


Figure 4 - Effect of liquid metal promoter (Bi) for catalytic performance in Fisher-Tropsch synthesis. Presence of Bi over surface of Fe carbide leads to oxygen scavenging facilitating dissociation of CO [6].

localized at the interface between metal nanoparticles. This shell provides continuous “washing” of the surface of metal nanoparticles.

The presence of Bi or Pb on the surface of Co results in the oxidation-reduction cycling during carbon monoxide hydrogenation and removal of deposited carbon and catalyst self-regeneration. Formation of the liquid metal layer at the surface of metal nanoparticles protects them also against sintering (figure 5).

The next example is devoted to a reaction of different kind, for which a different route has been found to be appropriate to achieve the promotion of a metal catalyst, namely the

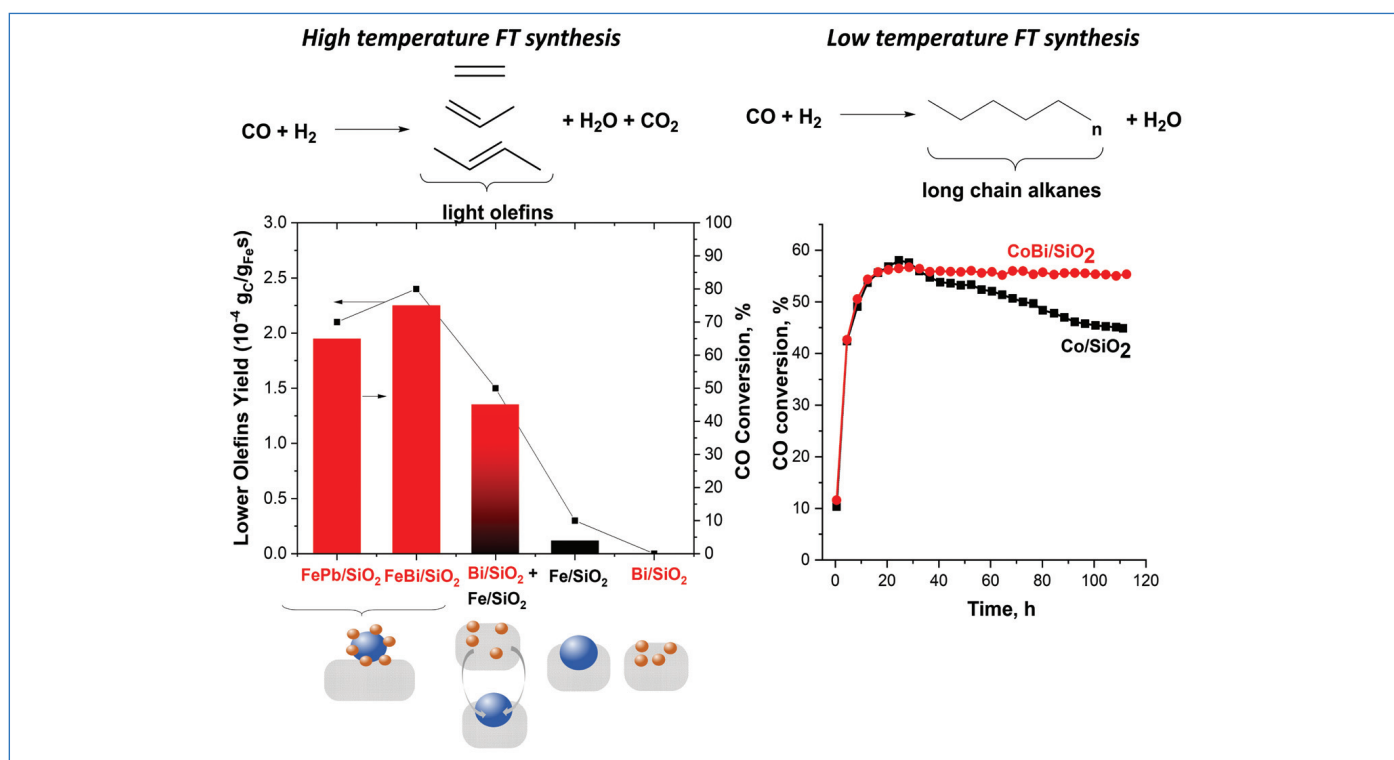


Figure 3 - Effect of liquid metal promoter for activity and stability in Fischer-Tropsch (FT) synthesis for high temperature (HT) and low temperature (LT). Presence of Bi or Pb leads to significant increase of the activity to light olefins in HTFT and stability in LTFT [6-8].

Carbon deposition for selective synthesis of primary amines

Amines are important platform molecules for chemical industry and life sciences. For instance, aliphatic amines and their derivatives are essential intermediates for the manufacture of agrochemicals, pharmaceuticals, organic dyes, detergents, fabric softeners, surfactants, corrosion inhibitors, lubricants and polymers. Primary amines can be prepared by different reactions, including Hoffman alkylation, Buchwald-Hartwig and Ullmann reactions, alkyl halide amination, hydroamination of olefins, hydrogenation of nitriles, and reductive amination of aldehydes/ketones [9]. Furthermore, primary amines can be synthesized by the direct amination of bio-based alcohols with NH_3 . Unlike aliphatic acids, esters, alkenes, ethers, and other reactants, alcohols and NH_3 are inexpensive and available substrates. Most importantly, the synthesis of primary amines can proceed at relatively mild conditions with water being the main by-product. This makes direct alcohol amination reactions economically efficient and environmental friendly.

The metal catalysts for the direct alcohol amination reactions operate *via* the so-called "hydrogen borrowing" mechanism relying on concomitant dehydrogenation and hydrogenation reactions. With the assistance of dehydrogenation-hydrogenation catalysts, mostly based on Ni, Co and Ru supported over alkaline or amphoteric metal oxides, alcohols can react directly with NH_3 to yield primary amines [10]. Current amination catalysts usually suffer from several drawbacks such as limited scope, use of high temperatures ($> 150^\circ\text{C}$), high NH_3 and H_2 pressures, undesired side reactions, including synthesis of secondary and tertiary amines by further reaction of primary amines. As a result, poor selectivity of primary amines is often obtained ($< 50\%$). The selectivity to primary amines sharply drops at higher alcohol conversion (*figure 6*) due to secondary and tertiary amines as side products.

Although catalyst deactivation is generally undesired, blocking some active surface sites may exert a positive effect on the catalytic performance. Indeed, deactivation can moderate the overall activity and/or improve the

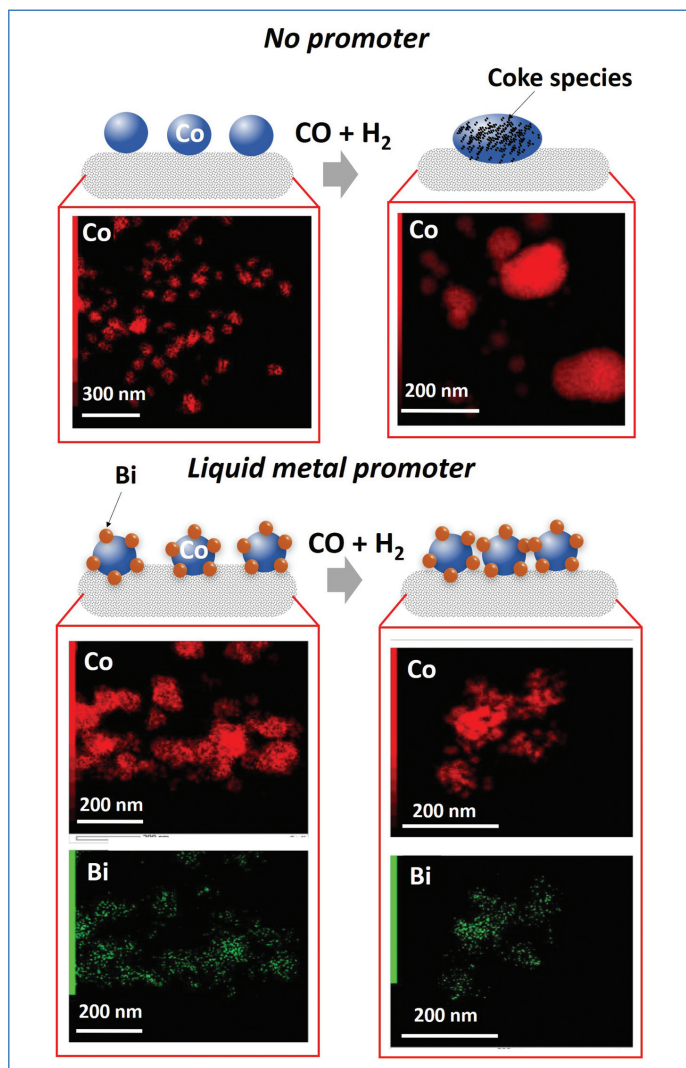


Figure 5 - Effect of liquid metal promoter on sintering of Co nanoparticles studied by TEM-EDX analysis. The presence of Bi promoter isolates metal nanoparticles and suppresses sintering of Co nanoparticles.

selective poisoning of the metal surface by carbon as non-metallic promoter for selective amination of alcohols to primary amines.

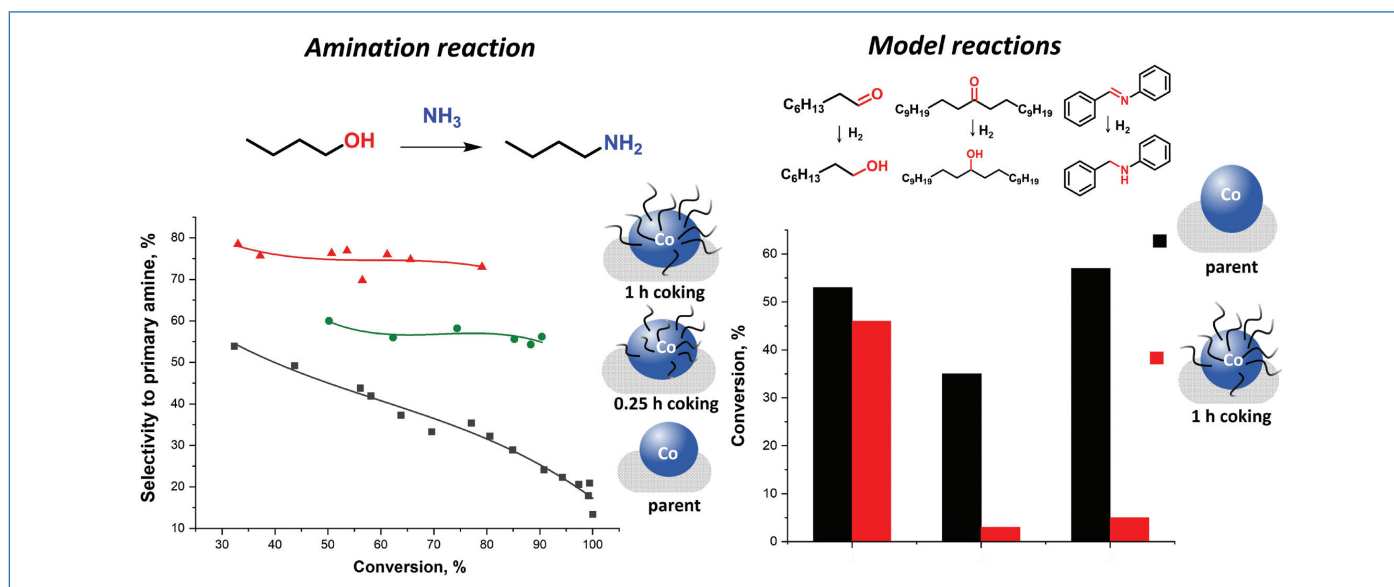


Figure 6 - Effect of carbon deposition for amination and model hydrogenation reactions. Carbon deposition over Co nanoparticles leads to increase of the selectivity to primary amines. The catalyst after carbon deposition provides high activity for transformation of primary chemicals [11].

In-situ carbon deposition

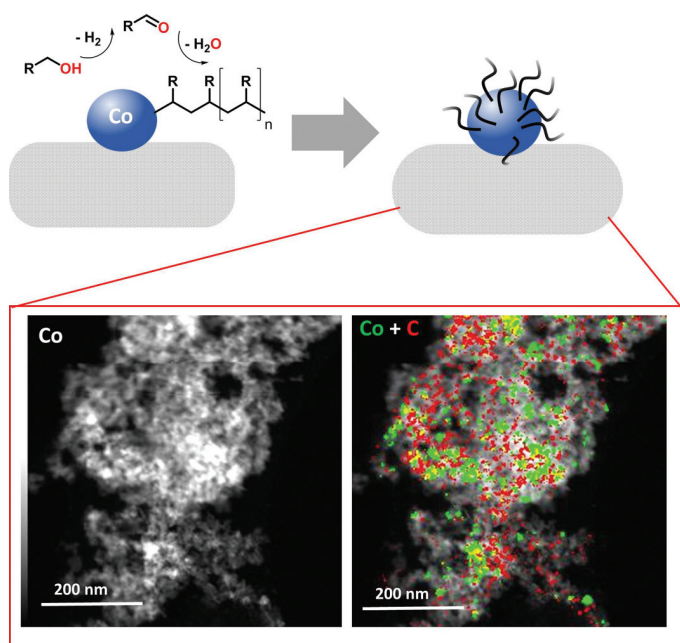


Figure 7 - In situ coke deposition technique and TEM analysis. Treatment of the catalyst in alcohol leads to deposition of polymeric carbon species over Co nanoparticles [11].

selectivity to the desired products due to deactivation of unselective active sites or structure/electronic effect of deactivation agent.

In the present example, intentional deposition of polymeric carbonaceous species on the surface of Co/Al₂O₃ catalysts was used to considerably improve the selectivity of alcohol amination to primary amines in the reaction of aliphatic alcohols with NH₃ both in gas and liquid-phase processes [11]. The catalysts were pretreated with alcohols at the temperature of the amination reaction (figure 7). Pretreatment in alcohol at 250 °C over the catalyst leads to dehydrogenation of alcohol with formation of highly reactive aldehyde, which immediately polymerizes over the metal surface with formation of carbon species specifically over Co metal surface according to TEM analysis.

The catalytic amination of alcohols using pretreated catalysts has demonstrated significant increase in the selectivity to

primary amines at comparable conversions of alcohols with increase in the time of treatment in alcohol and amount of deposited carbon species (figure 6).

The synthesis of primary amine proceeds by dehydrogenation of alcohol to aldehyde with subsequent non-catalytic reaction with ammonia for the synthesis of primary imine (figure 8). The formed imine might be hydrogenated to amine or react with another amine molecule with formation of secondary imine and ammonia. The possible role of deposited carbon species could be relevant to the suppression of hydrogenation of secondary imine to secondary amine. Deposition of polymeric species over cobalt nanoparticles should lead to the growth of the carbon polymeric layers around the domains of active metal sites and could result in formation of isolated cobalt domains. A possible explanation of the slow hydrogenation of secondary imines over the catalysts pretreated with alcohols could be steric hindrance effect, which inhibits the planar mode adsorption of bulky secondary imines in comparison with easier vertical adsorption of primary imines.

In order to confirm the strong influence of steric hindrances on the hydrogenation of bulky molecules, which might be created by carbon deposition, we have performed hydrogenation of model carbonyl compounds (tricosan-12-one, octanal) and secondary imine (N-benzylideneaniline) over the freshly activated catalyst and its counterparts with deposited carbon (figure 6).

Halogens are also often considered as poisons in heterogeneous catalysis. Their presence in the feed usually leads to the drop of the reaction rate. In the last example, we show that although iodine deactivates Pd in hydrogenation reactions, Pd-I species form acid site by activation of hydrogen for the reaction of etherification.

Iodine deposition for reductive etherification reaction over Pd

Ethers and its derivatives are widely used as solvent, surfactants, pharmaceuticals, polymers and liquid fuels. The reductive condensation of alcohols with aldehydes and ketones yielding ethers has been recently proposed as an innovative route to valorize bio-sourced platform molecules [12]. The reaction mechanism involves intermediate acetalization of a carbonyl group over an acid catalyst with subsequent

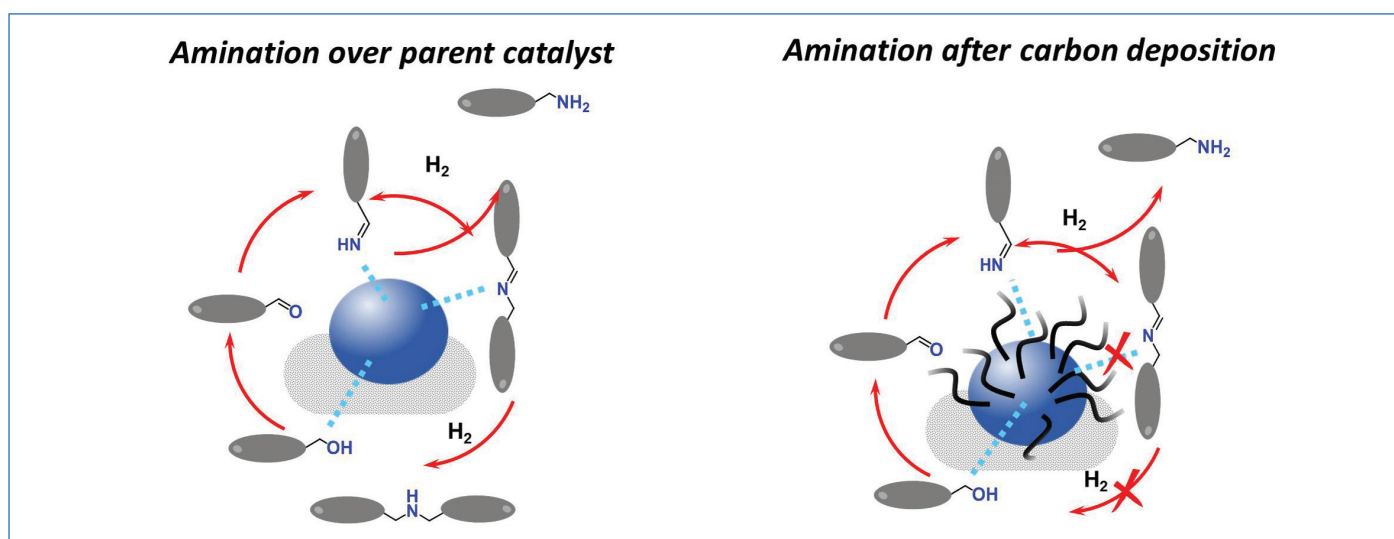


Figure 8 - Effect of carbon deposition for amination. Presence of carbon over metal leads to suppression of hydrogenation of secondary imine and increases the selectivity to primary amine [10-11].

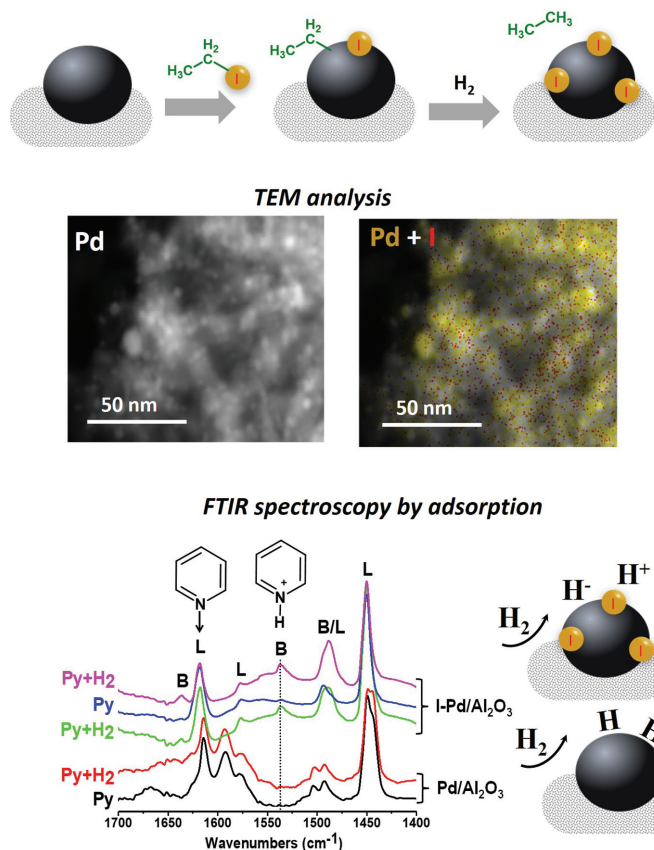


Figure 9 - *In situ* iodine deposition over Pd with analysis by TEM and FTIR spectroscopy. Figure demonstrates presence of iodine over Pd surface. In the presence of hydrogen, catalyst generates Brønsted acidity according to FTIR [14].

hydrogenolysis of the reaction intermediates to ethers over metal sites. The proximity of acid and metal sites in the bifunctional metal-acid catalysts is commonly enhanced by using liquid acids or their solutions (H_2SO_4 , HCl , etc.). However, poor selectivity, high temperature, low catalytic activity and difficult catalyst separation from the reaction products have been so far serious drawbacks for the implementation of reductive etherification in an industrial scale. Molecular iodine has been reported as an effective catalyst for the acetalization reactions [13], which have been widely used as a protection method for the carbonyl groups in organic synthesis. One of possible catalytic effects of iodine is related to the generation of hydrogen iodide, which acts in liquid solutions as a Brønsted acid and activates the carbonyl groups by hydrogen bonding. Promotion of metal-supported catalysts with iodine could be therefore favorable for the selective synthesis of ethers from aldehydes and alcohols, since both acetalization and hydrogenolysis functions will be combined in proximity over a single catalyst. Herein, we have developed a new extremely efficient Pd-I catalyst (figure 9) for reductive condensation of aldehydes and ketones with alcohols with high ether productivity and operating at very mild reaction conditions [14]. The catalyst described in this work can be prepared by "in situ" modification of a commercially available Pd-supported catalyst with organic iodide. This substantially simplifies its preparation process. The treatment of organic iodide with Pd-based catalyst in the presence of hydrogen results in dissociation of these compounds with formation of Pd-I species (figure 9).

To identify the presence of Brønsted acid sites, an *in situ* pyridine-FTIR analysis was carried out on Pd catalyst treated

by iodine (figure 9). After adsorption of pyridine, in the presence of hydrogen, appears peak related to the pyridinium ion (Py-H^+). This might indicate generation of Brønsted acidity on the catalyst under hydrogen atmosphere. Removal of hydrogen from the IR cell led to disappearance of this peak. Thus, the remarkable catalytic behavior of the I-Pd catalysts could be explained by the electronic interactions between the Pd and iodine species. After dissociation of hydrogen on the surface of Pd, a strong electron withdrawing effect of the neighboring iodine species could cause polarization of hydrogen over the Pd-I pairs. Because of the high negative charge, the adsorbed iodine atoms would favor stabilization of H^+ produced during hydrogen dissociation, resulting in the generation of Brønsted acidity. Catalyst demonstrates high stability without leaching of iodine species like HI during reaction. A feasible reaction pathway for the etherification of furfural and isopropanol on the bifunctional I-Pd/ Al_2O_3 catalyst is presented in figure 10. First, Brønsted acid sites (H^+) are produced on the sites of adsorbed iodine atoms *via* hydrogen dissociation on Pd-I sites. Then, the acetal intermediates are produced *via* nucleophilic addition of alcohol to aldehyde catalyzed by the Brønsted acid sites. Finally, the C-O bond dissociates with formation of water and addition of H from Pd surface to form ether. Thus, we could demonstrate that modification of Pd surface by iodine as promoter creates principally new active sites able to activate hydrogen in a heterolytic way for acidic reactions.

Towards new catalytic processes

Selective promotion of metal-based catalysts has shown strong effect on the catalytic performance for different reactions like Fischer-Tropsch synthesis, amination and etherification. Presence of a promoter of a kind that is well adapted to the reaction results in high activity, selectivity and stability of the catalyst. Depending on the kind of reaction, suitable promoters can be metallic, non-metallic or even carbon species produced during the reaction. The selective promotion of the catalyst active phase can be achieved using high mobility of promoters such as soldering metals or reactions of promoter precursors (e.g. carbon or

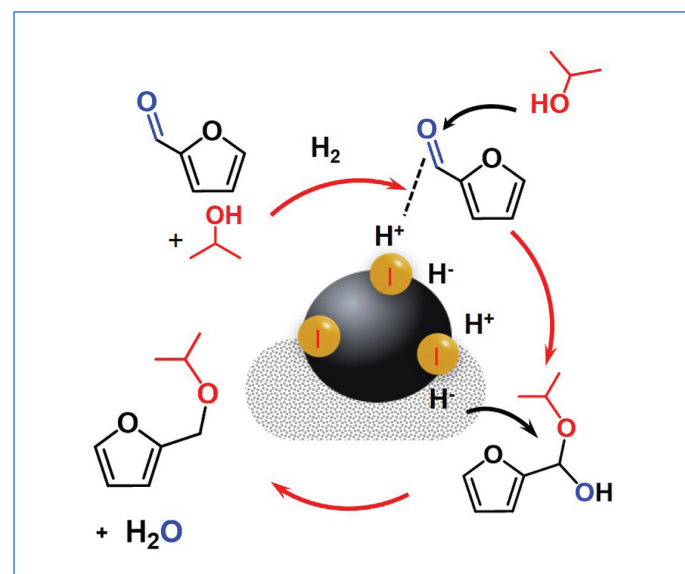


Figure 10 - Mechanism of etherification over Pd-I. Hydrogen adsorption over Pd-I species generates Brønsted acidity for acetalization and subsequent synthesis of ether [14].

iodine species) with metal nanoparticles. The catalytic effects of promoters can arise forming the following phenomena:

- catalytic assistance of promoters for activation of the reagents over metallic active phase, for example by oxygen scavenging;
- steric hindrance, which might be created by promoters in order to provide the specific environment around the active sites for selective catalytic performance;
- continuous refreshing of the metal surface by competition for the adsorption on the active phase between promoters and reacting molecules, isolation of metal nanoparticles and high catalyst stability;
- emergence of new active sites (for example Brønsted acid sites) due to the strong interaction between promoters and active phase.

Thus, a given promoter can be efficiently used for control of reaction rates, selectivity and catalyst stability in a given catalytic reaction. Specific catalytic effects are functions of the compatibility of promoter, the method of deposition and – importantly – reaction itself. Uncovering and identification of new promoters, their selective deposition and migration over the catalyst active phase should result in new efficient and sustainable catalytic processes for numerous branches of chemical industry.

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