



Preface

Catalyst-support interactions in heterogeneous catalysis: From fundamental concepts to applications



We are pleased to bring you this special issue of *Catalysis Today* compiling a selection of original papers and a review, focused on the role of supports in catalysis. High-surface area materials such as metal oxides, zeolites and carbon allotropes are commonly used in supported heterogeneous catalysis to improve the dispersion and thermal stability of the active phase. Far from being just physical carriers, supports play an important role in the determination of properties, structure, and functions of heterogeneous catalysts, by (partial) encapsulation, induction of strain and electronic effects, often referred to with the umbrella term “strong metal-support interactions” (SMSI). While advances in material science and characterization techniques have shed new light into the interactions of active phase and support at (and close to) their interface, much remains to be done to unravel the fundamentals of support effects and to leverage specific interaction by rational catalyst design.

The topics of this special issue cover the effect of supports in improving sintering resistance, enhancing catalytic activity and stability and tweaking catalysts selectivity in oxidation, hydrogenation, reforming and decomposition reactions. Many of the studies are focused on Pd or Ni active phases for the activation of small molecules, and on CeO₂- and TiO₂-supported catalysts, as reducible oxides are known to induce SMSI. Notable is also the attention given to zeolites as supports with controlled porosity and tunable acidity and structure, which can be leveraged to strongly anchor or encapsulate the active phase and to provide specific functional interfacial sites. We believe the present special issue brought together some of the excellence in the field of supported heterogeneous catalysis and we wish it will favor future discussion and inspire further work in the complex and yet exciting and promising field of interfacial catalysis. Below we provide a brief summary of the contributions in this special issue.

In the paper by H. Dai et al., highly active and poisoning-resistant acetylene combustion catalysts were produced by supporting IrFe bimetallic catalysts over mesoporous CeO₂. The enhanced performance was attributed to CeO₂ reducibility, which provided reactive oxygen via the so-called Mars-van Krevelen mechanism. Tuning strong metal-support interactions at the interface of iron oxide and hydroxyapatite, J. Wang et al. produced sintering-resistant and highly active Au nanocatalysts for CO oxidation and reverse water-gas shift. The key to achieve enhanced performance was anchoring Au nanoparticles at the interface between Fe₂O₃ and hydroxyapatite, inducing partial encapsulation on just one side of the particles, leaving the other side exposed to the gas phase. Y. Chen et al. provided insights into enhanced NH₃ self-catalytic reduction by tuning Ce-Zr oxide acidity introducing Mo and W oxides. Tungsten was found to be a better promoter, introducing more

Lewis acid sites, inducing active surface nitrate formation and resulting in improved deNO_x activity. F.-S. Xiao et al. reported an electronic metal-support interaction (EMSIs), involving charge transfer taking place between titanasilicate zeolites and Pt nanoparticles, which were tested for methanol steam reforming. The work shows that EMSIs can take place even on metals supported on zeolites containing heteroatoms, which opens new possibilities in catalyst design.

L. Olsson et al. studied structure-performance relationships in zeolite-supported Pd in the complete oxidation of methane. The authors showed that mobile Pd species led to the formation of ion-exchanged Pd and large Pd particles, both detrimental in methane oxidation catalysis. To preserve the highly active smaller Pd nanoparticles, the authors used zeolites with high Si/Al ratios, low Brønsted acidity and small pore sizes, which all decreased Pd mobility. Similarly, J. Wolska et al. showed that the acidity of Beta zeolite was pivotal in tuning Au nanoparticles size, and in turn in controlling the catalytic activity and selectivity in the base-free oxidation of glucose to gluconic acid. The zeolite acidity was further modified in order to avoid formation of glucuronic acid. P. Da Costa et al. also reported on better anchoring and dispersion of the active phase by tuning the support composition, in particular looking at Ni nanoparticles on CeO₂/SBA-15 added with yttrium, for enhanced catalytic CO₂ hydrogenation performance. Yttrium was found to increase CeO₂ and NiO reducibility, and to introduce more medium basic sites, favoring CO₂ adsorption during the reaction.

N. Semagina et al. contributed to this issue with a review focusing on support effects in Pd-catalyzed lean methane combustion in the presence of water, a common deactivating agent especially at low operating temperatures. The support reducibility, oxygen mobility, hydroxyl group stability and hydrophilicity/hydrophobicity were indicated as key factors to achieve high water resistance, mostly because of their effect on the evolution of Pd speciation (metallic, oxide or hydroxide) during the reaction. Furthermore, hydrothermal stability was discussed, with attention to zeolitic supports engineering and post-modification strategies. Methane combustion was also studied by A. Banerjee et al., focusing on the effect of calcination temperature on the structure and performance of Pd/Al₂O₃ catalysts. The observed activity trends were interpreted in terms of different Pd-alumina interfacial chemistry and a varying degree of Pd nanoparticles restructuring during reaction, both strongly depending on calcination temperature.

Inspired by experimental evidence of enhanced CO oxidation on intercalated Pd nanoparticles in layered TiO₂, G. Pacchioni et al. theoretically investigated the effect of interfacial contact between layered TiO₂ and different Pd nanostructures, namely intercalated or supported Pd nanoparticles and sandwiched Pd(111) slabs. In accordance with

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experimental results, the authors evidenced that Pd intercalation promotes SMSI, inducing structural changes and charge transfer from Pd to the oxide layers. Pd catalysts supported on oxygen- and phosphorus-functionalized carbon nanofibers for formic acid decomposition were studied by A. Villa et al., revealing an effect of functional groups at the metal/support interface on enhancing activity, and on inhibiting side reactions and leaching, thus improving catalysts selectivity and stability. Better leaching resistance was rationalized by theoretical calculations showing stronger Pd adhesion on functionalized graphene model surfaces.

A. Corma et al. provided a study on NiMo-S hydrotreating catalysts, showing experimental evidence of support effects in the hydrogenation of 1-methylnaphthalene. The authors ascribed the observed enhanced performance of NiMo supported on basic supports to an electronic enrichment of the active phase induced by electron transfer, in turn favoring the formation of S vacancies, for adsorption and activation of reactants. In the field of dry methane reforming (DMR), L.F. Liotta et al. reported on complex interactions of Ni with La-Ce binary oxides, leading to the formation of lanthanum nickelate phases, NiO or La oxide-decorated NiO particles, depending on La loading, which in turn strongly affected the catalytic activity in DMR. Finally, O. Kwon et al. studied the effect of different oxide perovskite thin films grown on MgAl₂O₄ on Ni performance in DMR, showing that LaMnO₃ maintained

a better Ni dispersion and thus resulted in less deactivation when compared to Ca, Sr and Ba titanate films.

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