



New insights into the role of the electronic properties of oxide promoters in Rh-catalyzed selective synthesis of oxygenates from synthesis gas

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ABSTRACT

A series of 2.5% Rh/M@Al₂O₃ model catalysts were prepared by supporting Rh on high-area γ -Al₂O₃, resulting in a surface covered by a monolayer (4.5–7 atoms/nm²) of MO_x promoter oxides (M = Fe, V, Nb, Ta, Ti, Y, Pr, Nd, Sm). The catalysts were extensively characterized and evaluated for the conversion of synthesis gas to oxygenates at 553 K, 5.0 MPa, H₂/CO = 1, and space velocity adjusted to attain CO conversion around 15%. The broad range of products formed depending on the specific promoter were, for the first time, quantitatively described using the *selectivity parameter* (Φ) defined here, which indicates, for a given reaction product, the contribution of carbon atoms derived from dissociative (C_{dis}) and nondissociative (C_{ins}) activation of CO. Both the catalytic activity and, more interestingly, the selectivity pattern given by the Φ parameter were correlated with the electronic properties of the MO_x promoters (i.e., electron-donating/electron-withdrawing capacity) for an extensive series of catalysts. *Low-temperature* and *at-work* CO-FTIR experiments suggested that the high activity and hydrocarbon selectivity displayed by catalysts promoted by more electron-withdrawing (acidic) oxide promoters (e.g., TaO_x) were related to a higher proportion of bridged Rh₂(CO)_B adsorption sites and to a higher electron density (i.e., a higher electron back-donation ability) of the Rh⁰ surface sites, both factors promoting CO dissociation events. In contrast, linear CO adsorption on Rh⁰ sites displaying decreased electron back-donation in catalysts promoted by electron-donating (basic) oxides (e.g., PrO_x, SmO_x) was likely related to nondissociative CO activation and thus to the selective formation of oxygenates. TEM, XPS, and CO-FTIR results pointed to differences in morphology, rather than size or partial electronic charge, of the nano-sized Rh⁰ crystallites as the likely cause for the different proportions of CO adsorption sites. The Rh⁰ NP morphology, both as-reduced and at-work, is a function of the electronic properties of the underlying promoter oxide.

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1. Introduction

Higher (C₂₊) oxygenates are highly demanded energy carriers and platform chemicals. For instance, the current ethanol market is witnessing a sparked growth, with a forecast worldwide production of around 60 × 10⁶ t/year in 2012, due to its applications as transportation fuel, source of renewable hydrogen for fuel cells, and feedstock for the synthesis of chemicals such as ethylene [1,2]. In addition, longer-chain (C₃–C₆) aliphatic alcohols hold great industrial interest as fuel additives, high-energy-density fuels, and raw materials for polymers and fine chemicals [3]. Moreover, carboxylic compounds such as acetic acid and methyl and ethyl acetates are valuable oxygenates that find application as raw chemicals and solvents in a wide range of industries, with a current combined world demand exceeding 8 × 10⁶ t/year.

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Dwindling crude oil reserves and concerns related to competition with the food industry are factors encouraging the development of effective catalytic processes to produce higher oxygenates from abundant and/or renewable resources, as an alternative to petroleum refining and edible-crop-consuming fermentative routes [4–6]. The catalytic conversion of synthesis gas (*syngas*) derived from stranded natural gas reservoirs or biomass (including lignocellulosic biomass) into higher oxygenates has long been known. Although the process has not yet been commercially implemented, renewed industrial and scientific interest is being experienced nowadays, as attested by considerable governmental and private strategic research investments.

Rh-based catalysts have been known to be effective for the selective synthesis of C₂₊ oxygenates (denoted hereafter as SSO) from *syngas* since the middle 1970s [7]. Although this catalytic system shows promise due to its high selectivity to linear C₂₊ oxygenates, particularly to ethanol, as well as to the fact that it does not require the presence of sulfur in the *syngas* feed stream,

its commercial application has been hindered mainly by the relatively low catalytic yields and the high cost and limited availability of Rh. Thus, a deeper understanding of the nature of active/selective sites, based on which novel optimized catalysts could be synthesized, seems crucial for improving the commercial competitiveness of the Rh-catalyzed SSO.

Apart from commercial considerations, the use of Rh-based catalysts for the SSO is of particular scientific interest due to a singular and drastic *promotion effect*, according to which the addition of transition metal or lanthanide oxides as promoters is essential to attain acceptable catalytic activity and selectivity to the desired oxygenates. It is known that unpromoted Rh nanoparticles (NPs) supported on the most common SiO_2 or Al_2O_3 carriers show low activity and very poor selectivity to oxygenates [8]. In contrast, the incorporation of promoters such as iron, either intentionally or coming from impurities in the support [9], dramatically changes the catalytic behavior by increasing the activity and selectivity to C_{2+} alcohols, especially ethanol. The search for the optimum promoter, or combination of promoters, has led to a vast amount of scientific work and several reviews during the past two decades [2,6]. For instance, Ichikawa [10,11] studied the promoting effect of several transition metal and lanthanide oxides in their dual role of promoter and catalytic support for Rh NPs and concluded that oxides displaying a slightly basic character (so-called *amphoteric oxides*) such as La_2O_3 , Cr_2O_3 , TiO_2 , and ThO_2 were the most effective in increasing the ethanol yield. On the other hand, Du et al. [12] found that among several lanthanide oxide promoters (La, Ce, Pr, Nd, and Sm), CeO_x and PrO_x lead to the highest ethanol selectivity in SiO_2 -supported Rh catalysts. More recently, Goodwin and co-workers [13] found a synergistic promoting effect of the combined addition of V and La oxides to a Rh/ SiO_2 catalyst, leading to higher CO hydrogenation activity and selectivity to ethanol (and in general to C_{2+} oxygenates) than for any of the monopromoted counterparts. In addition, some contradictory results can also be found in the previous literature dealing with promotion effects in Rh-catalyzed SSO. For instance, while some studies concluded that MnO_x was a suitable promoter for Rh in the SSO [14,15], others found that the addition of MnO_x to a Rh/ SiO_2 catalyst adversely affected its activity and selectivity to alcohols [16]. The complexity of the promoted Rh system is further evidenced by marked sensitivity of the selectivity pattern to subtle variations in the nature of the oxidic promoters. Thus, while Rh–Ir–Mn–Li/ SiO_2 catalysts displayed high selectivity to acetic acid [17], Rh–Fe–Mn–Li/ SiO_2 systems were shown to produce ethanol as the major oxygenate [18]. Similarly, Sachtler et al. observed a shift in the selectivity from acetic acid to ethanol as the major oxygenate upon incorporation of small amounts of iron into a Rh/NaY catalyst [19,20]. Besides its nature, the amount of oxidic promoter was also seen to impact the catalyst performance. Generally, both catalytic activity and selectivity went through a maximum with increasing promoter-to-Rh atomic ratio, which was interpreted in terms of decoration and, in the limit, occlusion of Rh NPs by the oxidic promoter phases [21]. Nevertheless, the adequate promoter/Rh ratio appears to be dependent on the specific catalytic system, since optimum Fe/Rh atomic ratios as disparate as 2.3 for Rh–Fe/ SiO_2 [22], 4.6 for Rh–Fe/ TiO_2 [22], and 9.2 for Rh–Fe/ Al_2O_3 [23] catalysts are reported, probably because of distinct levels of intimacy between the promoter and the Rh phase.

These results clearly point to the need for systematic studies aimed at elucidating the relationships between the nature of the oxidic promoters and the catalytic behavior, particularly the product selectivity. Gaining insight into the true role of catalytic promoters and their optimum electronic requirements will surely be crucial for the design of improved generations of Rh-based catalysts. Somorjai and co-workers [24] carried out an exhaustive study employing *inverse model* catalysts consisting of Rh⁰ foils sur-

face-decorated with patches of a transition metal oxide promoter for an extensive series of oxides (AlO_x , TiO_x , VO_x , FeO_x , ZrO_x , NbO_x , TaO_x , and WO_x) and found that the Lewis acidity of the promoter phase was crucial in determining the CO hydrogenation activity under methanation conditions and, thus, no consideration could be made in terms of product selectivity. Moreover, it has to be taken into account that in real catalysts Rh is present as a dispersed phase which, a priori, might behave differently than the Rh monocrystals in these *inverse model* catalysts.

It is widely accepted that the promoter/Rh boundary plays a key role in creating the required active sites for the SSO [24]. Thus, special care has to be taken in dealing with model catalytic systems to well define, and ideally maximize, the contact surface between these two phases, something which can hardly be controlled by employing conventional preparative techniques such as co-impregnation of Rh and the promoter's precursors. Additionally, the size of the metallic Rh NPs is another parameter to be considered, since it has been proved to influence the catalytic properties [25–27]. Hence, simply employing different metal oxides in the dual role of support and promoter will not generally lead to model catalysts displaying homogeneous metal dispersion, due to the great variability of textures among different oxides [28].

We present a systematic and exhaustive study on the effect of the electronic properties of oxidic promoters on the catalytic properties of model nanoparticulated Rh catalysts for the SSO. For the sake of homogeneity in their textural properties while maximizing the promoter–Rh contact boundary, the set of model catalysts was prepared by incorporating the Rh precursor onto high-surface supports consisting of a common porous carrier ($\gamma\text{-Al}_2\text{O}_3$) having its surface covered by a *monolayer* of the corresponding MO_x promoter oxide [23]. To attain a representative vision of the whole study space, a broad series of transition metal and lanthanide oxides (MO_x), displaying a wide range of electronic properties, were studied as catalytic promoters.

2. Experimental

2.1. Synthesis of catalysts

2.1.1. Synthesis of $\text{M@Al}_2\text{O}_3$ catalytic supports

The series of $\text{M@Al}_2\text{O}_3$ catalytic supports studied consisted of several metal oxides MO_x (where M = Fe(III), V(V), Nb(V), Ta(V), Ti(IV), Y(III), Pr(III), Nd(III), and Sm(III)) dispersed on the surface of $\gamma\text{-Al}_2\text{O}_3$. These materials were carefully prepared, targeting high dispersions for the MO_x species, ideally as bidimensional supported oxides, at surface coverages corresponding to *monolayer* saturation in each case. The common $\gamma\text{-Al}_2\text{O}_3$ carrier was obtained by calcination of high-purity commercial pseudo-boehmite, Pural-SB (Sasol Materials), at 773 K for 10 h in a muffle oven. Prior to the incorporation of metal precursors, the $\gamma\text{-Al}_2\text{O}_3$ carrier was dried at 423 K for 12 h.

The metal loading was adjusted in each case to attain nominal *monolayer* (ML) coverage on the $\gamma\text{-Al}_2\text{O}_3$ surface (based on the B.E.T. surface area of the dehydrated alumina of 205 m^2/g) by the MO_x promoter, according to previously published results where the ML saturation coverage was determined for several $\gamma\text{-Al}_2\text{O}_3$ -supported oxides [23,29–33]. These *monolayer* coverages were within the range of 4.5–5 M/nm^2 for most of the studied oxides, though in the case of VO_x , the required saturation coverage was 7 V/nm^2 due to the special packing of oxygen atoms in supported polyvanadates [29].

The loading of the $\gamma\text{-Al}_2\text{O}_3$ support with transition metal precursors (Fe, V, Nb, Ta, Ti, Y) was accomplished by impregnation with alcoholic solutions of organic precursors such as alkoxides or acetylacetonate (2,4-pentanedionate), which are the preferred

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