Catalysis Today 261 (2016) 17–27

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Hydrogen spillover in the Fischer–Tropsch synthesis: An analysis of platinum as a promoter for cobalt–alumina catalysts

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ARTICLE INFO

Article history:
Received 18 May 2015
Received in revised form 14 August 2015
Accepted 24 August 2015
Available online 9 October 2015

Keywords:
Hydrogen spillover
Hybrid catalysts
Noble metal promoter
TPR
TGA
In situ XRD
In situ XPS

ABSTRACT

Hydrogen spillover has been invoked to explain the functioning of platinum as a promoter in cobalt-based Fischer–Tropsch catalysts. In this study, the operation of Pt was investigated using a model hybrid catalyst (i.e. mixture of $Pt/Al_2O_3 + Co/Al_2O_3$) which allowed for decoupling of hydrogen spillover effects from those requiring direct Pt–Co contact. Pt improved the reducibility of the hybrid catalyst despite physical separation of Pt from Co.

TPR, TGA, in situ XRD and quasi in situ XPS confirmed that supported Co_3O_4 reduced via formation of CoO as a stable intermediate. Pt had only a slight effect on $Co_3O_4 \rightarrow CoO$ reduction, but greatly improved the $CoO \rightarrow Co^0$ reduction which was severely hindered by interaction with the alumina support. The catalysing effect of Pt on the reduction was attributed to H_2 dissociation and its subsequent spillover occurring more readily than direct H_2 activation by the cobalt oxides. During the Fischer–Tropsch reaction, the role of spillover hydrogen was again invoked to explain the higher TOF and enhanced selectivity towards CH_4 and paraffins. Spillover from Pt was proposed to induce a hydrogen-rich microenvironment that resulted in a 'cleansing' effect on the catalyst surface and an increase in the selectivity of hydrogenated products.

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1. Introduction

Cobalt-based catalysts for the commercial low-temperature Fischer–Tropsch reaction require activation in a reducing atmosphere to form the metallic active phase. A high extent of reduction of the cobalt oxide to the metal is desired to maximise the catalyst activity but is seldom achieved especially when using highly interacting supports like Al_2O_3. Some interaction between the support and the cobalt crystallites is crucial because it provides the anchorage required to prevent crystallites from migrating and sintering, and therefore helps to minimise the associated loss in catalytic activity. Unfortunately, strong metal support interactions (SMSIs) favour cobalt dispersion at the expense of reducibility, which results in the need for reduction promoters such as Pt in the commercial Al_2O_3-supported catalyst [1–14].

Platinum's ability to catalyse the reduction of cobalt oxides has been attributed to a high affinity for H_2 activation (i.e. adsorption and dissociation) although electronic/ligand effects arising from Pt–Co coordination may also occur. The proposed promotion mechanism(s) is therefore inadvertently linked to the promoter's location relative to the cobalt crystallites: Pt must coordinate directly with Co to induce an electronic effect, while it must be exposed to the gas phase to activate H_2 molecules that may subsequently spillover to the Co for reduction. Studies have shown that Pt–Co coordination occurs readily [5,9,10,12,15] and this could have non-trivial effects on the activity, deactivation, regeneration and the reduction of the oxide phase. On the other hand, reduction of cobalt oxides via a hydrogen spillover mechanism has been suggested for noble metal promoters [16–18]. The effects of hydrogen spillover from promoters are not limited to reduction, but have also been proposed to influence the CH_4 selectivity and cobalt activity during the Fischer–Tropsch reaction [13,19–21].

Scheme 1 illustrates the intrinsic steps that may occur during the reduction of a metal oxide in the presence of a noble metal promoter according to a hydrogen spillover mechanism. The process is initiated by dissociative adsorption of H_2 on the promoter surface (Step 1). This is followed by the spillover step during which hydrogen atoms cross the promoter–oxide interface (Step 2). Reduction may then occur when the spillover hydrogen atoms react with oxygen in the structure of the metal oxide to form water,

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http://dx.doi.org/10.1016/j.cattod.2015.08.050
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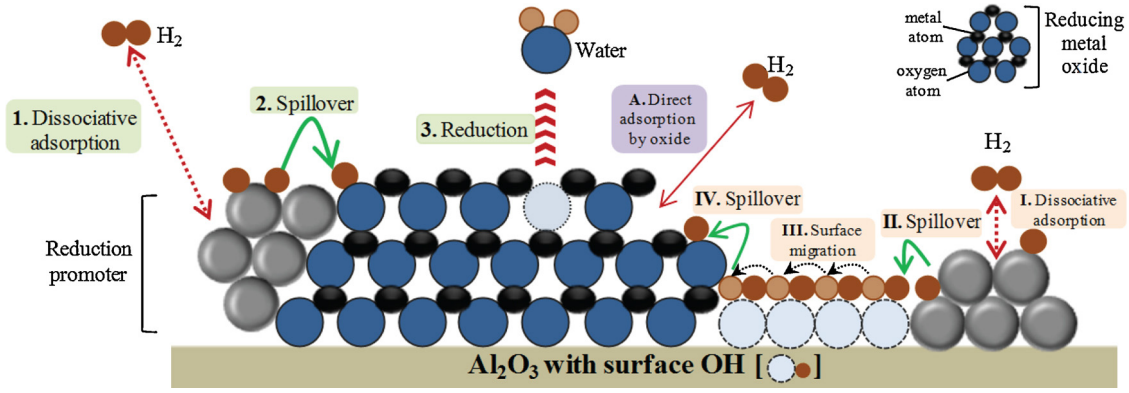
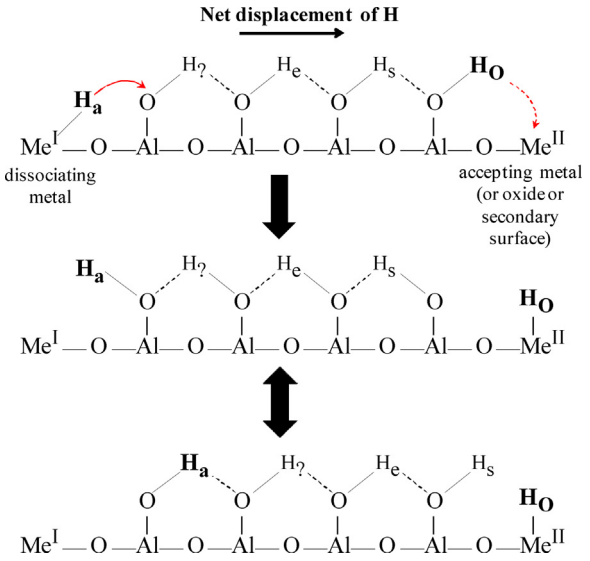


Scheme 1. Proposed pathway of spillover hydrogen during the promoter-aided reduction of a metal oxide.
Adapted from Conner and Falconer [30] and Luo and Epling [29].

leaving the metallic phase behind (Step 3). Alternatively, spillover can occur from an isolated promoter crystallite to the surface of the support (Step II). During this process, a strong hydrogen–metal bond is broken in favour of a bond/interaction with the receiving support surface. Surface migration of hydrogen atoms may then occur via the surface hydroxyl (OH) groups of the oxidic support (Step III). Finally, spillover from the support to the metal oxide may occur (Step IV), followed by reduction (Step 3). Reduction via spillover competes with direct H_2 adsorption at active sites of the cobalt oxides which are depicted as two adjacent metal atoms with an O vacancy (i.e. a defect) between them (Step A).

Migration distances of a few nanometres to several centimetres have been reported for spillover hydrogen species [17,18,22–27]. On oxidic surfaces such as Al_2O_3, surface diffusion of hydrogen species is reported to involve interaction with surface oxygen atoms or hydroxyl groups [17,25,28]. It has been suggested that hydrogen migrates by continuously forming and breaking adjacent OH bonds, but the energy barrier for this process is quite high [29]. A viable alternative explanation is the 'bucket-brigade' model in which surface OH groups do not migrate, but rather act as vehicles that pass along spillover hydrogen species. The interactions with hydrogen are proposed to be weak H···OH bonds and enable a process that has a low energy barrier and fast rates of surface diffusion. The bucket-brigade model has been directly referred to or inferred in a number of studies [24,29–31] and is illustrated in Scheme 2. The movement of hydrogen is analogous to the Grotthuss mechanism that governs the unusually high proton mobility in water via a network of hydrogen bonds [32]. Spillover hydrogen (H_α) from the dissociating metal (Me^I) migrates to a secondary surface (Me^{II}) for reaction via a hydrogen-bonded network of OH groups on the surface of an oxidic support. H_α transfers onto an O atom in its vicinity from where it is passed and received in an on-going exchange of covalent and hydrogen bonds between neighbouring OH groups [30]. When H_α crosses the metal–support interface to the closest surface OH group (see red arrow in Scheme 2), the effect is that H_Ω at the extreme end of the chain is 'pushed' out of the network towards Me^{II}. Consequently, the spilt over H_α does not physically migrate but rather triggers a knock-on effect that results in a net displacement of hydrogen. Mobility in this manner is high because it is the charge of the H_α that is transferred, rather than its mass.

The 'bucket-brigade' model accounts for the migration of hydrogen over oxidic surfaces such as catalyst supports. However, before this transportation can occur, a strong hydrogen–metal (H–M) surface bond must be broken to allow hydrogen species to spillover from the dissociating metal onto the support. This interfacial transfer is energetically hindered because of the high binding energy between hydrogen and metal surfaces [24,33]. Levy and Boudart [33] proposed that interfacial spillover occurred via formation of



Scheme 2. Illustration of the surface migration of hydrogen according to the bucket-brigade model/Grotthuss-type mechanism. ——, covalent bonds and other interactions; - - -, hydrogen bonds.
Adapted from Carley et al. [31].

a *solvated proton* when a co-catalyst with a high proton affinity such as water abstracted an adsorbed hydrogen atom from the dissociating metal surface to form a proton. The proton could then transfer easily to the site where it was required through a molecularly adsorbed co-catalyst monolayer. Formation of the proton was determined to be exothermic and compensated for the energy required to break the hydrogen–metal bond. Alternative pathways that have been suggested to govern interfacial spillover include: transfer of only weakly chemisorbed hydrogen atoms [34], 'jumpover' of activated hydrogen atoms via the gas phase [35] and 'bridges' such as carbon and specific interfacial OH groups at the metal–support interface [36–39].

The objective of this study was to explicate the effect of the Pt promoter on the alumina supported Co-based catalyst during reduction and at commercially relevant Fischer–Tropsch conditions using a model 'hybrid' catalyst. The hybrid catalyst was a mechanical mixture of $Pt/Al_2O_3 + Co/Al_2O_3$ catalysts which provided a means to isolate hydrogen spillover as a remote-control effect, from the ligand/electronic promoter effects that require physical contact between Pt and Co.

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