# CO bonding and hydrogenation activity of promoted noble metal catalysts during restructuring in high-pressure CO hydrogenation: $FeIr/SiO_2$

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Bimetallic $FeIr/SiO_2$ catalysts that are active for methanol production from synthesis gas ($CO + H_2$) bind CO less strongly, and exhibit higher activity for the hydrogenation of ethylene in the presence of CO, than catalysts that produce mainly methane. It is argued that promotion of the noble metal serves to weaken the adsorption of CO, thereby lowering its tendency to dissociate, and, most importantly, enhancing the surface coverage of hydrogen. Both factors are favorable for methanol formation.

**Keywords:** methanol synthesis, CO hydrogenation, bimetallic catalysts, Fe–Ir catalysts, ethylene hydrogenation

## 1. Introduction

Noble metals such as palladium, iridium and platinum are poor CO hydrogenation catalysts producing mainly methane [1]. However, the addition of metal oxide promoters significantly increases the activity of the noble metals for the $CO + H_2$ reaction and shifts its product distribution towards methanol and higher oxygenates, particularly at higher pressures (10 bar and up) [2].

Bimetallic catalysts of the type Fe–Rh, Fe–Pd, Fe–Ir, and Fe–Pt on silica and other supports form a special class of active and methanol-selective CO hydrogenation catalysts, and have received a great deal of attention in the past 20 years [3–13]. Previous work from our laboratory showed that Fe–Ir and related catalysts prepared by impregnation initially produce methane and need typically some 24 h on stream before they fully exhibit their favourable activity for methanol [5,6].

The nature of the beneficial promoting effect of all these additives to the noble metal is not yet entirely understood. Explanations are usually given in terms of the stabilization of noble metal ions [14], or the presence of noble metal–promoter ion combinations [8,15]. The way CO adsorbs on these promoted surfaces is thought to open the way for straightforward reaction pathways to methanol. Recent results on temperature-programmed $H_2$ desorption from cluster-derived $FeIr/SiO_2$ catalysts by Marengo et al. [13], however, suggest that the interaction of hydrogen with the promoted surface is a key factor as well.

The purpose of this paper is twofold. First we apply in situ infrared spectroscopy to show that the Fe–Ir catalyst in its active state for methanol production binds CO weaker than the same catalyst in its initial, methane selective state. Second, we use hydrogenation of ethylene in the presence of CO as a test for the hydrogenation activity of the catalyst. The latter experiments indicate that methanol-selective Fe–Ir catalysts possess significantly higher hydrogenation activities than either unpromoted Ir or bimetallic Fe–Ir in the methane productive state do. In a subsequent paper we investigate the structural changes of Fe–Ir catalysts that accompany the changes in catalytic behavior [16].

## 2. Experimental

$FeIr/SiO_2$ catalysts were prepared by incipient wetness impregnation of $SiO_2$ (Grace 332, 270 $m^2/g$, pore volume 1.6 ml/g) with solutions of $Fe(NO_3)_3 \cdot 9H_2O$ (Merck p.a.) and $IrCl_3 \cdot nH_2O$ (Johnson Matthey Chemicals, 54% Ir). Unless indicated otherwise, the total metal loading of the catalysts was 5 wt%. After impregnation, the catalysts were dried in air at 110°C for 16 h.

Reactions were carried out in a stainless-steel fixed-bed reactor. CO was led over a silica column at 300°C in order to decompose metal carbonyls, and dried over a 4 Å molecular sieve. Hydrogen was dried, and used without further purification. Catalyst samples (250 mg) were reduced in hydrogen at 450°C for 1 h and tested at 270°C and 40 bar in a 4 Nℓ/h syngas flow ($H_2/CO = 3$). Products were analyzed by a gas chromatograph with a flame ionization detector. Ethylene hydrogenation was measured at atmospheric pressure in a 1.5% ethylene/syngas mixture.

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Infrared spectra of adsorbed CO were measured with a Mattson Galaxy single-beam spectrometer equipped with a DTGS detector. Measurements were carried out in an IR cell which allows for in situ catalyst pretreatments at temperatures up to 600°C and pressures up to 30 bar. A sample containing 20 mg of catalyst was pressed into a wafer of 13 mm in diameter and used for the infrared experiments. The sample was reduced in situ in flowing hydrogen at 450°C for 1 h. The catalyst was then exposed to 2 bar of $H_2$/CO at 50°C for 1 min, or to 30 bar of syngas at 275°C until steady-state was reached. The observed activity per gram of catalyst and the methanol selectivity during CO hydrogenation in the IR cell were comparable to the results of experiments in the normal reactor. Spectra were measured during temperature-programmed desorption of CO at a heating rate of 5°C/min, and a pressure$\leq 6.10^{-2}$ mbar. All spectra are averages of ten scans at 1 $cm^{-1}$ resolution, taken during a 1.5 min interval.

## 3. Results

### 3.1. CO hydrogenation

Figs. 1 and 2 summarize the main properties of FeIr/$SiO_2$ catalysts in the CO hydrogenation. Methanol and methane are the main reaction products [4–6]. However, methane is produced from the beginning of the reaction, while the production of methanol starts low and increases gradually. Depending on pressure and on metal loading, the CO conversion over freshly reduced catalysts reaches steady-state during activation periods of at least 12 h. An exception is the 1 : 5 FeIr catalyst, which is stable from the beginning. The standard experiment in our research used a 5 wt% 1 : 1 FeIr catalyst at 40 bar, which took about a day to reach steady state, whereafter it remained stable for weeks (the longest period tested was 4 weeks). During the activation period, a new type of site appears to be formed which is active for the formation of methanol. No significant changes are observed with respect to the formation of hydrocarbons.

### 3.2. Infrared spectroscopy

In situ infrared spectroscopy has been used to monitor differences in the desorption of CO from freshly reduced, *i.e. methane-selective*, and activated, *methanol-selective*, Fe–Ir catalysts. The infrared spectra of CO on Ir/$SiO_2$ and FeIr/$SiO_2$ consist predominantly of peaks in the range 2000–2075 $cm^{-1}$, and are characteristic of linearly adsorbed CO. A detailed description of the infrared studies has been given elsewhere [17].

Fig. 3a shows the FTIR spectra of the freshly reduced FeIr/$SiO_2$ catalyst after exposure to 2 bar of $H_2$/CO at 50°C for 1 min, and heating to the indicated temperature under vacuum. The peak at 2060 $cm^{-1}$ corresponds to the linear CO species that are usually observed on the noble group 8 metals, while the peak at 2000 $cm^{-1}$ is thought to be associated with a linear CO species interacting with adsorbed water [17]. The intensity decrease of the latter, which is accompanied by a slight intensity increase of the 2060 $cm^{-1}$ peak upon heating the sample under vacuum to 100°C, would be in agreement with this interpretation. Upon heating further, the CO signal decreases, indicating that CO desorbs from the surface. Note that the infrared intensity is at best a qualitative measure for CO coverage, as dipole–dipole interactions have a profound influence on infrared absorption; in extreme cases they may even lead to a decrease in intensity with increasing coverage [18,19].

The same experiment was repeated with an activated FeIr/$SiO_2$ catalyst which had been pretreated in 30 bar of CO/$H_2$ at 275°C until steady-state activity had been reached. As fig. 3b shows, desorption of CO from the activated Fe–Ir catalyst occurs at significantly lower temperatures than desorption from a freshly reduced catalyst. Although comparison of absolute infrared intensities between different samples is difficult, the

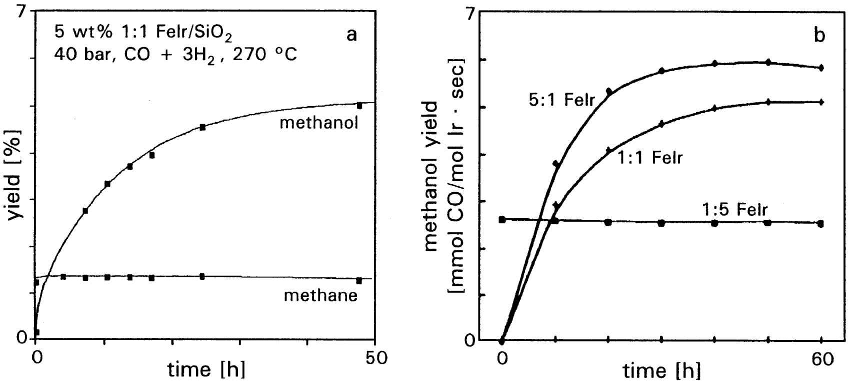

Fig. 1. (a) Conversion of CO into methane and methanol versus time on stream over a 5 wt% 1: 1 FeIr/$SiO_2$ catalyst (40 bar of 3 $H_2$ + 1 CO synthesis gas at 270°C). (b) CO conversion into methanol over FeIr catalysts of different composition.

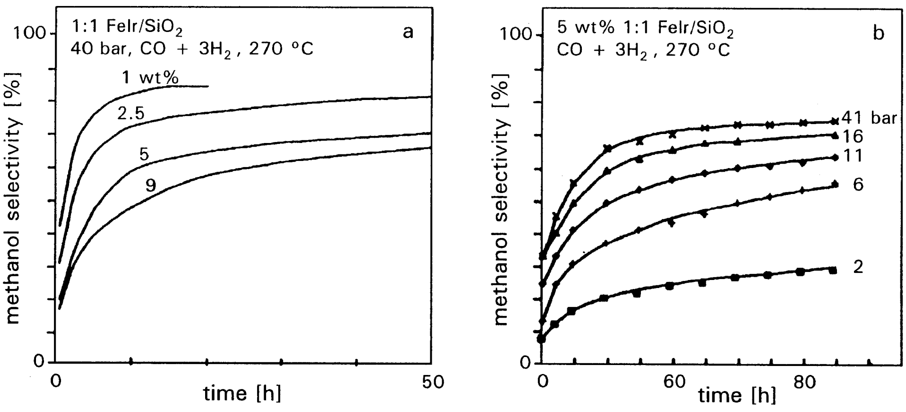

Fig. 2. Methanol selectivity of 1 : 1 FeIr/$SiO_2$ catalysts (in 3 $H_2$ + 1 CO synthesis gas at 270°C) versus time on stream, (a) as a function of total metal loading at 40 bar, and (b) as a function of total pressure (metal loading 5 wt%).

spectra contain no evidence that the CO adsorption capacity of the activated catalyst differs very much from the fresh one. Thus, the results clearly indicate that CO adsorbs less strongly on activated FeIr/$SiO_2$ than it does on a freshly reduced catalyst.

### 3.3. Ethylene hydrogenation

Ethylene hydrogenation in the presence of CO was used as a test reaction for the hydrogenation activity of the catalysts during methanol formation. Fig. 4 shows the ethylene hydrogenation activity of a monometallic Ir/$SiO_2$ catalyst and two bimetallic FeIr/$SiO_2$ catalysts, all after initial reduction and after activation. During the experiment the temperature was ramped at 1°C/min.

The fresh and spent monometallic Ir/$SiO_2$ and the fresh 1 : 1 FeIr/$SiO_2$ have a low hydrogenation activity. The interesting point to note is that the spent 1 : 1 FeIr/$SiO_2$ catalyst, i.e. in the state active for methanol production, possesses a greatly increased hydrogenation activity in comparison to the freshly reduced catalyst. Another remarkable result is that the 1 : 5 FeIr/$SiO_2$ catalyst, which is active for methanol production from the beginning of the CO hydrogenation, has a high hydrogenation activity already in the freshly reduced state. The results of fig. 4 thus strongly suggest that a catalyst having high hydrogenation activity, has a high activity for methanol production as well.

## 4. Discussion

Supported bimetallic Fe–Ir catalysts are active for the synthesis of methanol from synthesis gas. Fe–Ir catalysts derived from organometallic clusters [7,8,13] and those prepared by impregnation but with a low iron content (Fe : Ir = 0.2 or smaller) are active for methanol formation from the beginning, while Fe–Ir catalysts of

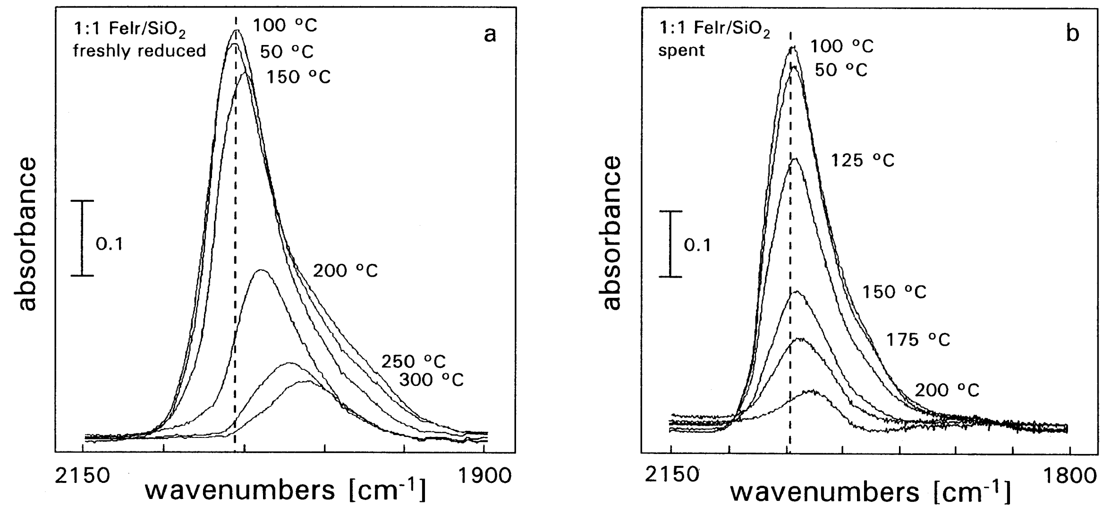

Fig. 3. Infrared spectra of CO adsorbed on FeIr/$SiO_2$ during temperature-programmed heating (rate 5°C/min); (a) freshly reduced catalyst; (b) activated after treatment in 30 bar of CO/$H_2$ at 275°C.

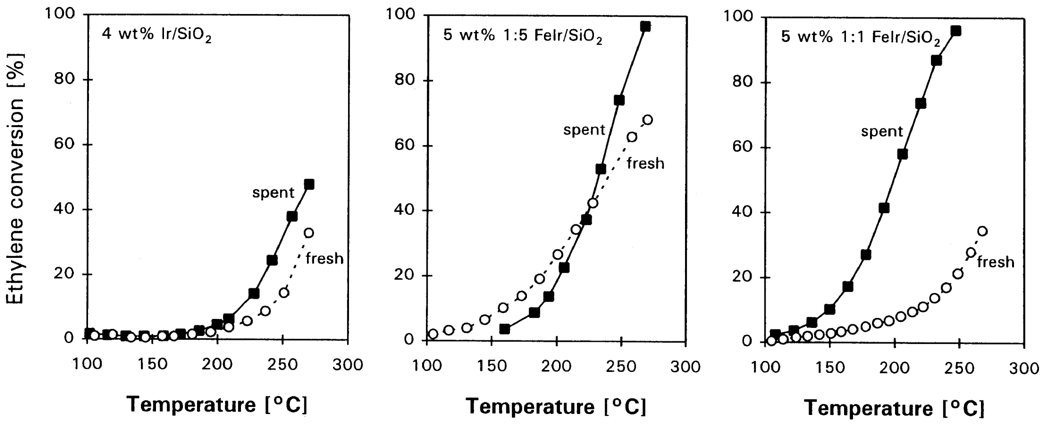

Fig. 4. Temperature-programmed ethylene hydrogenation in the presence of CO for freshly reduced (dashed lines) and spent (solid lines) Ir and FeIr catalysts. Conditions: 1.5% ethylene in 1 bar of CO+ 3H$_2$; heating rate 1°C/min.

higher iron content develop this property during the first 12–24 h on stream [5,6]. The present results reveal a clear correlation between methanol selectivity, activity for ethylene hydrogenation in the presence of CO, and a reduced bond strength for CO adsorption, pointing toward increased hydrogen coverage as a key factor for methanol formation.

The fresh 1 : 1 FeIr/SiO$_2$ catalyst has a low activity both for methanol synthesis and for ethylene hydrogenation. After activation, however, when the 1 : 1 Fe–Ir catalyst has reached its favorable activity for methanol production, it is also significantly more active for ethylene hydrogenation. Interestingly, the fresh 1: 5 FeIr/SiO$_2$ catalyst, with its high initial activity for methanol [5] also has a high hydrogenation activity. The Ir/SiO$_2$ catalyst is the least active in both methanol synthesis and ethylene hydrogenation, both after initial reduction and prolonged use in CO hydrogenation. Thus, the surface active for methanol synthesis is capable of hydrogenating ethylene in the presence of CO. As ethylene hydrogenation (in the absence of CO) occurs readily on most group 8 metals [20], we believe that the hydrogenation activity of the Fe–Ir catalysts is associated with the adsorption strength of CO and thus to the extent that the hydrogenation is poisoned by adsorbed CO. Support for this view is provided by the infrared studies of CO desorption in fig. 3: an activated Fe–Ir catalyst in its methanol producing state binds CO less strongly than the catalyst in its methane producing form. This implies that the methanol-selective surface not only has a lower tendency to dissociate the CO bond [21] but also has the ability to accumulate a higher hydrogen coverage.

Interestingly, several results in a recent publication by Marengo et al. [13] on cluster-derived FeIr/SiO$_2$ catalysts also point to the interaction of hydrogen with the surface as a key factor. Temperature-programmed desorption runs indicate that H desorbs from Fe–Ir catalysts at temperatures that are significantly higher than desorption from Ir-only catalysts. Preadsorbed CO hydrogenates at lower temperatures on the bimetallic catalysts. Finally, kinetic measurements indicate orders negative in CO and positive in H$_2$ for methane formation, but for methanol formation the order in CO is slightly positive and that in H$_2$ positive, but lower than for methane formation [13]. All these findings are in agreement with the notion that promotion of the noble metal iridium by the non-noble iron leads to increased hydrogen coverages on surfaces active for methanol formation.

We therefore propose that methanol formation occurs from a CO that is adsorbed on a monometallic iridium site, modified by the presence of iron. The promoting effect of the latter is attributed to a weakening of the Ir-CO bond strength (and possible stronger bonding of hydrogen as well), resulting in an increased hydrogenation activity of the promoted surface.

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