Methanol from synthesis gas over bimetallic FePd catalysts

Citation for published version (APA):

Niemantsverdriet, J. W., Grondelle, van, J., & Kraan, van der, A. M. (1988). Methanol from synthesis gas over bimetallic FePd catalysts. *Hyperfine Interactions*, 41(1-4), 677-680. <https://doi.org/10.1007/BF02400481>

DOI:

[10.1007/BF02400481](https://doi.org/10.1007/BF02400481)

Document status and date:

Published: 01/01/1988

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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METHANOL FROM SYNTHESIS GAS OVER BIMETALLIC FePd CATALYSTS

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Bimetallic FePd/SiO₂ catalysts exhibit higher activities in the formation of methanol from synthesis gas than Pd/SiO₂. The catalysts are a complex mixture of bcc and fcc FePd alloy, α -Fe and some unreduced iron.

1. INTRODUCTION

At present the production of fuels from synthesis gas is economically unattractive. The reaction to oxygenates, however, remains a viable application of CO + H₂ chemistry. The performance of Rh, Pd, and Ir catalysts in the oxygenate synthesis at elevated pressures (2-7 MPa) can be improved by adding a second metal such as iron /1-4/. In this paper we show that Fe enhances the activity of SiO₂-supported Pd for methanol formation. Mössbauer spectroscopy and X-ray photoelectron spectroscopy (XPS) show that the FePd/SiO₂ catalysts are a complex mixture of bcc and fcc FePd alloy, α -Fe and some unreduced iron.

2. EXPERIMENTAL

Catalysts were prepared by adding dropwise an aqueous solution (pH=1) of PdCl₂ (Merck p.a.) and Fe(NO₃)₃·9H₂O (Baker) to the SiO₂ support (Aerosil 300V, 300 m²/g) until incipient wetness. Three different catalysts were prepared, 5 wt% Pd/SiO₂, 1:1 FePd/SiO₂ with 3.3 wt% Pd and 1.7 wt% Fe (10% enriched in ⁵⁷Fe), and 1:5 FePd/SiO₂ with 4 wt% Pd and 0.4 wt% Fe (90% ⁵⁷Fe). Samples were dried in air at 295 K for 72 h, at 320 K for 18 h, and at 400 K for 72 h. After reduction, CO hydrogenation was carried out in a copper-coated stainless steel reactor in 3 H₂ + CO (GHSV = 4000 /h, 1 ml catalyst, density 0.47 g/ml) at 4.0 MPa (gauge) and 545 K.

Mössbauer spectra were obtained in situ as described elsewhere /5/. Spectra were fitted with calculated subspectra consisting of Lorentzian-shaped lines by varying the Mössbauer parameters (IS, QS, H, ϵ' , Γ , and area) and the background parabola coefficients in a non-linear, iterative minimization routine /6/.

3. RESULTS AND DISCUSSION

Combination of iron and palladium in a bimetallic catalyst enhances the CO hydrogenation activity, while the favorably high methanol (MeOH) selectivity of Pd is retained (Fig. 1 and Table 1). Unfortunately, the most active catalyst, 1:1 FePd/SiO₂, deactivates severely (Fig. 1a). An interesting feature of the 1:1 FePd/SiO₂ catalyst is that it develops its MeOH selectivity during the first 8 hours of the reaction. A similar slow activation has been observed with iron-rich FeIr/SiO₂ catalysts /4/.

Fukushima et al. /3/ report MeOH selectivities below 50% for FePd/SiO₂ catalysts with Fe/Pd ratios higher than 0.33. Our 1:1 FePd/SiO₂ catalyst, however, has a favorable MeOH activity of 82%, provided we wait for steady state conditions. The reason for the apparent discrepancy is most probably that the data in ref. /3/ have been obtained after a relatively short time of 4 hours /2/. As our results show, iron-rich FePd and FeIr/SiO₂ /4/ catalyst may not yet be at steady state after such a short time.

Fig. 1. Methanol (MeOH) from synthesis gas over Pd/SiO₂ and FePd/SiO₂ catalyst. a) MeOH yield per mole of the precious metal Pd, and b) Selectivity of the 1:1 FePd/SiO₂ catalyst during the first 12 hours of synthesis. The selectivities of 1:5 FePd/SiO₂ and Pd/SiO₂ are at a steady state level of 95 and 92% MeOH, respectively.

Table 1. Steady state selectivities in % of converted CO of FePd/SiO₂ catalysts in CO + 3H₂ at 545 K and 4 MPa.

Fe/Pd	CH ₃ OH	CH ₄	C ₂ +	DME	MeAc
0	92.3	3.1		3.4	
0.2	95.0	2.5		1.6	
1	82.3	9.0	3.7		4.1
Fe 3 wt%	13.5	33.0	40	-	-

C₂+: ethane and higher hydrocarbons, DME: dimethyl ether, MeAc: methyl acetate.

The Mössbauer spectra of Fig. 2 show that the reduction of iron is strongly catalyzed by Pd. The Fe³⁺ of the fresh FePd catalysts is already reduced to Fe²⁺ by H₂ at 295 K and Fe⁰ is formed at temperatures as low as 400 K, as indicated by the large single peak at 0.5 mm/s in the spectrum of 1:5 FePd/SiO₂. XPS shows that all Pd is already reduced at 295 K.

The catalysts reduced at the usual temperatures of 700 - 800 K contain iron in several different states. Table 2 list the results of curve fitting. The main differences between 1:1 and 1:5 FePd/SiO₂ are that the spectrum of the former contains iron predominantly in α -Fe (H=334 kOe) and bcc FePd (H=280 kOe), whereas the fcc FePd singlet (IS = 0.47 mm/s) prevails in 1:5 FePd/SiO₂. The parameters of FePd are in the ranges reported in ref. /7/, the differences in composition are in line with the FePd phase diagram /8/.

Fig. 2. In situ Mössbauer spectra at 295 K of initially fresh 1:1 and 1:5 FePd/SiO₂ catalysts after a series of subsequent reductions in H₂ for 1 hour at the indicated temperatures. The composition of the bottom spectra is given in Table 2.

It is interesting to compare the present results on FePd catalysts and those obtained with FeIr and FePt catalysts. All three catalysts systems exhibit high methanol selectivities (> 70%) in the CO hydrogenation at 4 MPa [2-4,9]. Fukushima et al [2] have suggested that ionic iron acts as promoter for the noble metals in methanol synthesis. Indeed, Mössbauer spectra indicate that a significant fraction of the iron in FeIr and FePt/SiO₂ catalysts remains un-reduced [5]. Nevertheless, evidence exists that in iron-rich FeIr/SiO₂ reduced iron is also involved in the sites which catalyze the reaction to methanol [9].

The situation in FePd/SiO₂ is different. Here almost all iron is present in the zero-valent state. Hence, it seems likely that the beneficial effect of iron on the methanol selectivity should be attributed to its presence in an FePd alloy. A note of caution is appropriate, however. We cannot exclude that during reaction, zero-valent iron in the surface of the FePd, FeIr and FePt alloy particles is oxidized due to water, a by-product of the CO hydrogenation. Hence, the question whether ionic or metallic iron is required for the formation of methanol from CO and H₂ can only be answered when Mössbauer spectra of FePd, FeIr and FePt catalysts are measured in situ after the CO + H₂ reaction at high pressure. Such measurements will be undertaken in the near future.

Table 2. Mössbauer parameters of iron in FePd/SiO₂ catalysts after reduction in H₂ at 800 K.

iron state	IS	QS mm/s	H kOe	ϵ' mm/s	Γ	area %
1:1 FePd/SiO ₂						
Fe ⁰ in bcc FePd	.47		280	-0.03	.96*	43
Fe ⁰ in fcc FePd	.47				.75	8
Fe ⁰ in α -Fe	.29		334	0.0	.47	45
Fe ²⁺	1.24	1.54			.72	4
1:5 FePd/SiO ₂						
Fe ⁰ in bcc FePd	.51		263	-0.05	.94*	24
Fe ⁰ in fcc FePd	.42				.52	40
Fe ⁰ in α -Fe	.26		333	0.0	.37	14
Fe ²⁺	1.40	1.47			.90	12
Fe ³⁺	.64	1.10			.60	10

* Linewidth outer lines; Accuracies: IS: 0.04 mm/s; QS: 0.07 mm/s; H: 3 kOe; ϵ' : 0.04 mm/s; Γ : 0.10 mm/s; area: 5%; IS relative to SNP.

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