Moessbauer spectroscopy of supported bimetallic catalysts: 1:5 FeM/SiO₂ (M = Ru, Rh, Pd, Ir, Pt)

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MÖSSBAUER SPECTROSCOPY OF SUPPORTED BIMETALLIC CATALYSTS:

1:5 FeM/SiO₂ (M = Ru, Rh, Pd, Ir, Pt)

J.W. NIEMANTSVERDRIET*, J. VAN GRONDELLE* and A.M. VAN DER KRAAN¹

**Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, Eindhoven, The Netherlands*

¹Interuniversitair Reactor Instituut, Delft, The Netherlands

Mössbauer spectra of SiO₂-supported bimetallic FeM (M = Ru, Rh, Pd, Ir, and Pt) with FeM = 1:5 after treatments such as reduction, exposure to CO and passivation in air are described and compared with previous results obtained on 1:1 FeM/SiO₂ catalysts.

1. INTRODUCTION

Alloying of metals provides a powerful means to optimize the performance of catalysts /1/. As catalysts should preferably have a large fraction of surface atoms, small-particle alloys stabilized by an inert support such as SiO₂ are of great practical interest. Mössbauer spectroscopy is an almost ideal technique to investigate iron-containing bimetallic catalysts, as the catalysts can be studied in the gaseous environments in which they are active.

We have previously investigated silica-supported bimetallic catalysts which contain equal molar amounts of iron and one of the more noble group VIII metals Ru, Rh, Pd, Ir, and Pt, abbreviated 1:1 FeM/SiO₂ /2-6/. In this contribution we report on the state of iron in FeM/SiO₂ catalysts with an Fe:M ratio of 1:5.

2. EXPERIMENTAL

Catalysts were prepared according to the incipient wetness technique, details in /6/. All catalysts contained 4.5 wt% of metal (Fe+M) with atomic ratio Fe:M=1:5. The iron was 10% enriched in ⁵⁷Fe. The support used was SiO₂ (Cab-o-Sil, EH-5, 310 m²/g). Impregnated samples were dried in air at 295 K for a week, at 330 K for 24 h, and at 400 K for 72 h. The dispersion of the catalysts was determined by H₂ chemisorption at 295 K according to Benson and Boudart /7/.

Mössbauer spectra were measured with a constant acceleration spectrometer, with the sample in the in situ reactor described previously /8/. Isomer shifts are reported with respect to SNP.

3. RESULTS AND DISCUSSION

Figure 1 shows the Mössbauer spectra of the 1:5 FeM/SiO₂ catalysts after reduction in H₂ at 725 K.

The Mössbauer spectra of the reduced FeRu, FeRh, and FePt catalysts could all be analyzed straightforwardly as a combination of subspectra of zero-valent iron in the FeM alloy, and a doublet of Fe³⁺ (Table I), similarly as in the corresponding 1:1 FeM/SiO₂ catalysts. For a detailed discussion of the Mössbauer parameters we refer to /6/.

The spectrum of 1:5 FePd/SiO₂ shows mainly the singlet of fcc FePd and two magnetically split contributions of α -Fe and of bcc FePd alloy /9/. To obtain an acceptable fit in the centrum of the

Fig.1. Mössbauer spectra at 295 K of reduced 1:5 FeM/SiO₂ catalysts.

spectrum, the presence of doublets for Fe³⁺ and Fe²⁺ has to be invoked.

The spectrum of 1:5 FeIr/SiO₂ is rather poorly resolved. We prefer to discuss the 1:5 FeIr/SiO₂ spectrum at a later occasion, when spectra taken at cryogenic temperatures will be available.

The dispersion, i.e. the fraction of Fe + M atoms located at the surface, of the 1:5 FeM/SiO₂ catalysts is between 27 and 88%. As a consequence, it may be expected that the Mössbauer spectra of such systems are affected by their gaseous environment. Figure 2 shows that this is indeed the case.

When reduced or passivated FeRu, FeRh and FePt on SiO₂ are exposed to CO gas at room temperature, significant fractions of the Fe³⁺ ions present are converted into Fe²⁺, as is indicated by the appearance of a new peak in the spectra around 2.5 mm/s. The fact that this transition of Fe³⁺ to Fe²⁺ takes place at room temperature is taken as evidence that the ions involved are exposed to the gas phase. As this CO-induced conversion of Fe³⁺ to Fe²⁺ has not been observed in monometallic Fe/SiO₂ catalysts, it stands to reason that these ions are located on the support, in the periphery of the alloy particles. Evidence for such an arrangement has been presented by our group for 1:1 FeM/SiO₂ catalysts /4,6/ and by Minal et al. /12,13/ for FeRh/SiO₂ catalysts with a wide range of Fe:M ratios.

Chemisorption of CO on 1:5 FePd/SiO₂ did not induce detectable changes in the Mössbauer spectra (not shown). As the Fe³⁺ content of this system is rather small, the absence of a detectable Fe³⁺ to Fe²⁺ transition under CO is, of course, not unexpected.

On exposing the 1:5 FeM/SiO₂ catalysts to air at 295 K, a considerable fraction of the zero-valent iron becomes oxidized to the Fe³⁺ state. Subsequent exposure of these air-passivated catalysts to

Fig.2. Mössbauer spectra at 295 K of bimetallic catalysts after reduction at 275 K, and subsequent exposure to CO, air and again CO at 295 K.

H₂ at 295 K results in the reduction of the ferric iron to zerovalent iron in the alloy. An exception is the FeRu/SiO₂ catalyst, in which reduction of the Fe³⁺ proceeds no further than to Fe²⁺. The remarkable reduction of Fe³⁺ in passivated catalysts at 295 K has been reported before by Garten /11/, and is regarded as the most direct evidence for the influence of the noble metal on the iron in these catalysts.

A remarkable result of the Mössbauer investigations of FeM/SiO₂ catalysts is the high Fe³⁺ content of reduced samples, in spite of the presence of a noble metal which is thought to promote the reduction of iron /2-6, 12-16/. We note that the presence of Fe³⁺ in reduced 1:1 FeRh/SiO₂ /5/ and 1:1 FeIr/SiO₂ /15/ has been adequately confirmed by in situ Mössbauer spectra at cryogenic temperatures, and in 1:5 FeRu/SiO₂ and 1:5 FePt/SiO₂ by in situ electron spin resonance /16/.

In conclusion, 1:5 FeRu, FeRh, and FePt on SiO₂ behave similarly as the corresponding 1:1 FeM/SiO₂ catalysts. The differences between 1:5 and 1:1 FePd/SiO₂ are predominantly due to a difference in crystallographic structure of the FePd alloy as predicted by the phase diagram. Further clarification of the Mössbauer spectra of the 1:5 FeIr/SiO₂ system remains necessary.

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Table 1
Dispersions and Mössbauer parameters of 1:5 FeM/SiO₂ catalysts

catalyst	H/M	IS mm/s	QS mm/s	H kOe	%	assigned to
FeRu	.27	.27	.19		16	hcp FeRu
		.69	.71		84	Fe ³⁺
FeRh	.88	.38			62	fcc FeRh
		.59	.81		38	Fe ³⁺
FePd	.38	.42		263 332	36	fcc FePd
		.49			23	bcc FePd
		.26			14	α-Fe
		1.41	1.48		15	Fe ²⁺
		.64	.85		12	Fe ³⁺
FeIr	.28			see text		
FePt	.82	.56	.43		17	FePt
		.69	.76		83	Fe ³⁺

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