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The influence of the chlorine content on the bimetallic particle formation in Pt–Re/Al_2O_3 studied by STEM/EDX, TPR, H_2 chemisorption and model reaction studies

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Abstract

A Pt–Re/Al_2O_3 reforming catalyst with different levels of chlorine content prior to reduction has been studied by various techniques such as combined STEM/EDX, TPR, H_2 chemisorption and model reactions in order to investigate the effect of the chlorine content on the bimetallic particle formation. TPR, H_2 chemisorption and model reactions show that chlorine inhibits the formation of bimetallic particles in the Pt–Re/Al_2O_3 catalyst. The effect of chlorine is, however, limited. Direct measurements by STEM/EDX analysis could not reveal any significant differences in alloy formation by varying the chlorine content from 0.6 to 1.5 wt.%. In comparison, the effect of adding water during reduction has a greater impact on the final state of the metal particles. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the introduction of the Pt–Re(S)/γ–Al_2O_3–Cl catalyst in catalytic reforming [1], this system has been extensively studied with regard to the role of rhenium. This is a bifunctional catalyst where platinum is the active hydrogenation/dehydrogenation catalyst, and the acidic support catalyses the isomerisation and cracking reactions. The acidity is adjusted by adding chlorine. Over time the bimetallic catalyst loses its activity especially due to coking. The addition of rhenium to the monometallic Pt/Al_2O_3–Cl catalyst increases its stability, but the way that rhenium modifies this system is not clear. It seems to be a general agreement [2–6] that rhenium has to be present “alloyed” with platinum in small bimetallic particles in order to have a beneficial effect. In industrial units sulphur is added to the catalyst in order to suppress undesired reactions. After a certain time on stream, the catalyst has to be regenerated by burning off the coke. Under these conditions platinum will sinter, and in order to re-establish the platinum dispersion and to restore the acidity of the support, the catalyst undergoes oxychlorination treatment followed by reduction. It has been reported that the chlorine level prior to reduction is critical for the alloy formation, but the conclusions are diverse. Michel et al. [7] suggest that there is a mobile rhenium oxychloride involved in the reduction mechanism, whereas others [8–9] claim that chlorine inhibits Pt–Re interaction. We have previously studied the

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formation of bimetallic particles on the Pt–Re/Al_2O_3 catalyst employing STEM/EDX, TPR, H_2 chemisorption and model reactions with respect to the pre-treatment conditions [10,11]. Evidence for alloy formation was found and it was shown that alloy formation was influenced by the drying temperature prior to reduction. The present study is aimed at investigating the effect of the chlorine content on the bimetallic particle formation in the same catalyst system.

2. Experimental

2.1. Catalysts

The catalyst used was EUROPT-4 (Akzo) 0.3–0.3 wt.% Pt–Re/γ–Al_2O_3. As received it contained approximately 1.0 wt.% Cl. To adjust the chlorine level, the catalyst was subjected to oxychlorination treatment at 500°C by using a flow of air saturated with different ratios HCl/H_2O. Finally, the catalyst was dried in air at 510°C. The chlorine content of these samples was measured to be 0.6, 1.1, and 1.5 wt.%, respectively, by Escha dissolution and silver nitrate titration using chromate as indicator (Mohr method). Before performing the catalyst test reaction, the catalyst was reduced from 200 to 480°C at 0.8°C/min and held at 480°C for 1 h in dry or moist (5000 ppm H_2O) hydrogen. The sample with the lowest chlorine content was called sample 1, whereas the samples containing 1.1 and 1.5 wt.% chlorine were named samples 2 and 3, respectively. When reduced in moist hydrogen, the same samples are referred to as samples 4, 5, and 6, with 0.6, 1.1, and 1.5 wt.% Cl prior to reduction, respectively.

2.2. Model reactions

Hydrogenolysis has been used as a probe reaction to distinguish between different degrees of alloy formation [12]. As reactants, *n*-butane and cyclopentane were used separately. The hydrocarbon/hydrogen mixture (molar ratio of 1/17 for *n*-butane and of 1/12 for cyclopentane) was pulsed (1.2 ml) over the catalyst bed (0.15 g) with regular intervals in a helium flow (250 ml/min) with a reactor temperature of 250 and 270°C, respectively. The product was analysed on-line using an HP 5890 series II gas chromatograph equipped with a flame ionisation detector (FID). The hydrocarbons were separated on a 50 m GC alumina column (J&W Scientific).

2.3. Temperature programmed reduction

Temperature programmed reduction (TPR) was used to further examine the degree of alloy formation of the Pt–Re catalyst. The TPR instrumentation has been described elsewhere [13]. 0.5 g of catalyst sample was heated slowly at 0.8°C/min, and dried at 510°C for 4 h. The TPR runs were performed with a heating rate of 10°C/min to 900°C, using a mixture of 7% H_2 in Ar (30 ml/min). The hydrogen consumption was monitored by a thermal conductivity detector (TCD).

2.4. Hydrogen chemisorption

Volumetric hydrogen chemisorption was measured at 25°C using a Micromeretics ASAP 2010 Chemi instrument. The samples were dried, reduced, and analysed in the chemisorption apparatus after oxychlorination treatment ex situ. The dispersion, or hydrogen to platinum ratio (H/Pt), is calculated based on the volume of hydrogen chemisorbed on the sample. The volume adsorbed was obtained by making two subsequent isotherms with evacuation to 10^{-5} torr for 30 min in between. The values reported in Table 1 were obtained by subtracting the second isotherm from the first isotherm. It is assumed that the adsorption stoichiometry for H_2 on Pt is $H/Pt = 1$, and that Re does not chemisorb H_2 at 25°C [14,15].

2.5. STEM/EDX particle analysis

Combined STEM/EDX particle analysis was performed at Lehigh University with a VG microscope

Table 1
Conversion of *n*-butane on the Pt–Re/Al_2O_3 catalyst containing different levels of chlorine (average values expressed in molar units)[a]

Sample	Chlorine level	*n*-Butane conversion (%)	C_1 selectivity	H/Pt
1	0.65	16	36	0.43
2	1.10	17	39	0.43
3	1.50	11	26	0.59

[a] Temperature = 250°C, $C_4/H_2 = 1/17$. Reduction in dry H_2.

HB-603. The particle sizes were found from the STEM images, whereas the EDX data yielded information on the composition. Detailed description of the analysis procedure is given elsewhere [11].

3. Results and discussion

3.1. Model reactions and hydrogen chemisorption

The results from the hydrogenolysis of *n*-butane performed on samples 1, 2, and 3 are presented in Table 1, and the data given is from the first pulse. The selectivity to methane is taken as a measure of the degree of Pt–Re interaction, and it can be observed that the sample with the highest chlorine content show the lowest activity for *n*-butane conversion and selectivity to methane. Sample 2 shows a slightly higher selectivity to methane than sample 1, but the difference is hardly significant. As sample 3 displays the lowest selectivity, it appears that the chlorine content of the catalyst prior to reduction has a significant effect on the final state of the metal phase. The presence of platinum and rhenium in intimate contact yields more active sites for hydrogenolysis than clusters of the respective atoms alone due to electronic interaction between the metal atoms. Hydrocarbons adsorb strongly on Re, but weaker on Pt. In such bimetallic clusters an intermediate heat of adsorption will result, giving the highest rate of reaction and methane formation. Reactions on the acidic support, such as cracking, will also occur but the hydrogenolysis reaction and the formation of methane is catalysed by the metal sites. When comparing the methane selectivity of catalysts with various chlorine content care has to be taken in order to account for the additional cracking activity of the acid sites. However, the conversion of *n*-butane is similar for samples 1 and 2 and even lower for sample 3. The difference in catalytic performance is therefore attributed to differences in the metal particle characteristics.

The results from the hydrogen chemisorption studies are also presented in Table 1 and they show that sample 3 adsorbs significantly more hydrogen than samples 1 and 2. Assuming that the dispersion is the same for all samples a possible interpretation for this behaviour is that a higher degree of alloy formation results in a lower H/Pt ratio. In an alloy fewer contiguous platinum atoms are present allowing less dissociative hydrogen chemisorption to take place.

Table 2
Conversion of cyclopentane (CP) on the Pt–Re/Al_2O_3 catalyst containing different levels of chlorine prior to reduction (average values expressed in molar units)[a]

Sample	Chlorine level	CP conversion (%)	C_1 selectivity
1	0.65	2.7	2.2
2	1.10	3.6	1.7
3	1.50	3.1	1.5

[a] Temperature = 270°C, $CP/H_2 = 1/12$. Reduced in dry H_2.

In order to obtain bimetallic particles it is important that the rhenium oxide species present on the surface may be able to migrate to the platinum atoms which have already been reduced. Rhenium oxide in intimate contact with platinum will then be catalytically reduced resulting in alloy formation. The interpretation of the results presented in Table 1 is therefore that a too high surface concentration of chlorine will possibly inhibit the mobility of the rhenium species resulting in lower degrees of alloy formation.

Table 2 shows the results from cyclopentane hydrogenolysis, and again the results indicate that the catalyst with the lowest level of chlorine has the highest degree of Pt–Re interaction. In this case sample 1 shows a higher selectivity to methane even though the conversion of cyclopentane is lower than for samples 2 and 3. This could be due to acid catalysed cracking reactions of samples 1 and 2 due to the promoting effect of chlorine.

The catalysts were also reduced in moist H_2 in order to study the effect of water on the reduction process. As all catalyst samples were dried at 510°C in air prior to reduction they are relative dehydrated [10]. From Table 3, it can be observed that the conversion of cyclopentane and the selectivity to methane increased

Table 3
Conversion of CP on the Pt–Re/Al_2O_3 catalyst containing different levels of chlorine prior to reduction (average values expressed in molar units)[a]

Sample	Chlorine level	CP conversion (%)	C_1 selectivity
4	0.65	7.8	5.9
5	1.10	5.5	5.0
6	1.50	7.0	5.0

[a] Temperature = 270°C, $CP/H_2 = 1/12$. Reduced in moist H_2.

for all catalyst samples when 5000 ppm of water is being introduced together with hydrogen during the reduction process. This increased activity can be explained by a higher degree of alloy formation due to an increased level of hydration during reduction as the presence of water in the form of hydroxyl groups increases the mobility of surface rhenium oxide species.

Sample 4, which contains the lowest amount of chlorine prior to reduction in moist hydrogen, shows the highest conversion of cyclopentane and the highest selectivity to methane. When discussing the effect of chlorine content on alloy formation under these conditions it has to be beared in mind that high temperature treatment in moist atmosphere introduces some stripping of chlorine. Hydroxyl groups will replace the surface chlorine atoms and thus both enhance the mobility of rhenium oxide by ensuring a higher level of surface hydration and reducing the inhibiting effect of chlorine. The sample with the lowest chlorine level will in this case also contain most bimetallic particles after reduction. The catalytic performance of all samples will be affected by the removal of chlorine as the acidity of the support will be altered. In spite of this the conversion of cyclopentane is higher after reduction in moist hydrogen and the increased conversion must be attributed to a higher degree of alloy formation. Water in the reduction gas could also lead to sintering of platinum, but as the structure sensitive hydrogenolysis reaction is favoured on small metal particles this effect is not significant.

Both *n*-butane and cyclopentane hydrogenolysis studies indicate that the chlorine level has an effect on the alloy formation. The selectivity to methane is highest for all samples containing the lowest amount of chlorine, also when water is added to the reduction gas.

3.2. STEM/EDX

The metal particles can be observed as diffuse white spots on the annular dark-field STEM micrograph. Information about the composition of the particles was obtained by collecting EDX-spectra of 100–120 particles for each sample. Particle composition — size diagrams, such as the ones shown in Figs. 1–4 were made for all samples.

The metal particles of the Pt–Re/Al_2O_3 catalyst are very small (≤2 nm). This makes direct studies

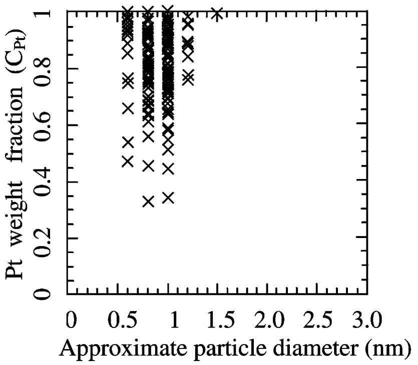

Fig. 1. Approximate particle diameter and measured Pt fraction of individual metal particles in sample 1 (0.65 wt.% Cl, dry reduction).

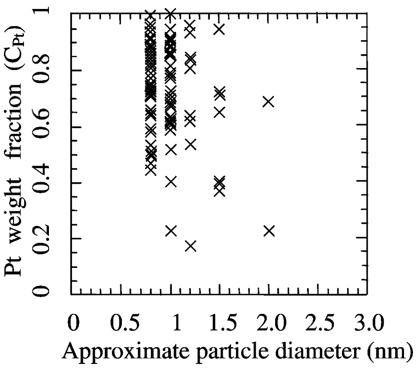

Fig. 2. Approximate particle diameter and measured Pt fraction of individual metal particles in sample 3 (1.50 wt.% Cl, dry reduction).

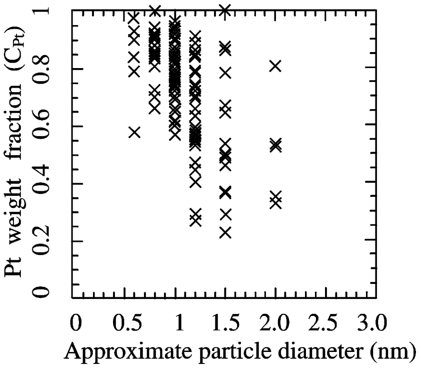

Fig. 3. Approximate particle diameter and measured Pt fraction of individual metal particles in sample 4 (0.65 wt.% Cl, moist reduction).

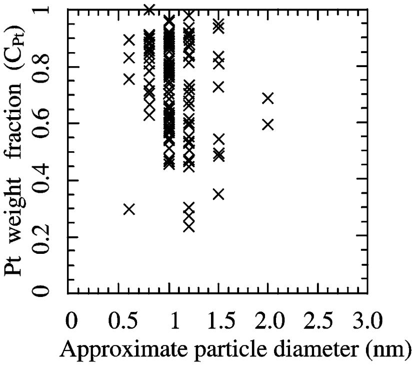

Fig. 4. Approximate particle diameter and measured Pt fraction of individual metal particles in sample 6 (1.50 wt.% Cl, moist reduction).

of the metal sites very difficult due to the resolution limitation of conventional instruments. Previous studies [16] using combined STEM and EDX to describe the Pt–Re alloy formation for the same catalyst system, have indicated that no rhenium was alloyed with platinum. However, it seems that the particles studied in this case were too large (2–3 nm) to represent the system. The instrument used here (VG Microscope HB 603) has been specially designed for high spatial resolution [17], and studies of particles smaller than 1 nm are possible.

Figs. 1–4 show the composition — size diagrams obtained from the STEM/EDX analysis of samples 1,3,4 and 6. The average particle size and the average metal composition were calculated for each sample based on the data collected from the STEM/EDX analysis, and are given in Tables 4 and 5. These results give an indication of the state of the metal particles on the catalyst after reduction. The average particle size and the particle composition are approximate values as indicated by the broad distribution of the parameters. It is therefore not obvious to find any trends from these data. It can be concluded that the effect of the chlorine level on the bimetallic particle formation is rather limited and therefore difficult to observe using this technique. The lack of significant results can also be attributed to various factors such as a limitation in the number of particles analysed. However, by comparing the shape of the composition — size diagrams in Figs. 1 and 3 it can be observed that the particles are somewhat larger and more alloyed when water is added to the reducing gas. It can be speculated that the effect of moisture in the reduction gas is the formation of larger particles. As previously discussed, water ensures rhenium oxide mobility and platinum sintering which results in larger particles as observed.

Table 4
Average platinum compositions (C_{Pt}) and particle sizes ($D_{particle}$) obtained from combined EDX/STEM analysis of the Pt–Re/Al_2O_3 catalyst containing different levels of chlorine (reduction in dry H_2)

Sample	Chlorine level	EDX, C_{Pt}	STEM, $D_{particle}$ (nm)
1	0.65	0.8	0.9
2	1.10	0.8	1.0
3	1.50	0.7	1.0

Table 5
Average platinum compositions (C_{Pt}) and particle sizes ($D_{particle}$) obtained from combined EDX/STEM analysis of the Pt–Re/Al_2O_3 catalyst containing different levels of chlorine (reduction in moist H_2)

Sample	Chlorine level	EDX, C_{Pt}	STEM, $D_{particle}$ (nm)
4	0.65	0.7	1.1
5	1.10	0.7	1.2
6	1.50	0.7	1.1

The results presented in Table 4 show that there is no significant individual difference between samples 1 and 3. This is as expected from observations of the composition — size diagrams shown in Figs. 1 and 2. After reduction of the dry (510°C in air) oxychlorinated samples in moist (5000 ppm H_2O) hydrogen, the STEM/EDX data presented in Table 5 indicate that the average particle diameter is larger than when reducing in dry hydrogen and a higher degree of alloy formation is present. The composition — size diagrams of samples 4 and 6 are presented in Figs. 3 and 4. The effect of water can be interpreted as being beneficial for the mobility of rhenium oxide species as previously discussed. However, it is not possible to find significant differences in alloy formation with varying chlorine content. As discussed previously, the introduction of water may introduce some stripping of chlorine, and this will also effect the formation of bimetallic clusters during reduction. The influence of water can thus be both ascribed to the removal of chlorine and to the

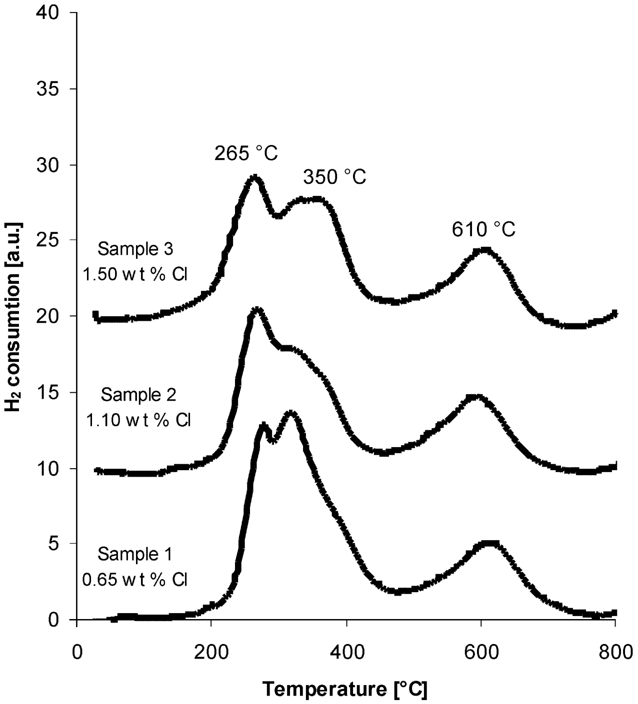

Fig. 5. TPR profiles of Pt–Re catalyst with different chlorine content. Sample 1: 0.65 wt.% Cl, sample 2: 1.10 wt.% Cl and sample 3: 1.50 wt.% Cl.

introduction of more hydroxyl groups on the catalyst surface. Both effect the mobility of rhenium, and thus the alloy formation.

3.3. TPR

From the TPR profiles in Fig. 5, it is observed a first peak at about 250°C which can be assigned to the reduction of Pt. At 350°C an other peak, or shoulder appears which is a characteristic of further reduction of Pt and the catalytic reduction of Re by Pt. The further reduction of rhenium can be seen as a peak at 610°C. Samples 1–3 differ in their TPR profile. Sample 1, with the lowest chlorine level, has the narrowest and largest peak in the low temperature region. Samples 2 and 3 have a lower H_2 consumption in this area reflected by the smaller peaks. This is as an indication of more formation of alloyed particles on sample 1 with the lowest chlorine level. Measurements of H_2 consumption and calculation of the degree of reduction of the metals are complicated by the fact that there might be some reduction and removal of chlorine. However, according to Barbier et al. [18] the chlorine level is approximately constant at low concentrations. Using the monometallic Pt catalyst (CK 300) as a standard, and assuming 100% reduction, the degree of reduction of Re can be calculated (both the co-reduction with Pt and the reduction at 610°C) by subtracting the hydrogen consumed by Pt. Re in sample 1 is reduced to ca. 80%, whereas the reduction degree of samples 2 and 3 is as low as 30%. The difference is reflected in the different size of the first peaks in the low temperature region. A higher degree of reduction of rhenium in the low temperature region in sample 1 can be interpreted such that this catalyst contains more alloyed particles than samples 1 and 2.

4. Conclusions

Using different experimental techniques, the effect of the chlorine content prior to reduction on the bimetallic formation in the Pt–Re/Al_2O_3 catalyst has been studied. Indirect methods such as model reactions, hydrogen chemisorption, and TPR studies indicate that too much chlorine on the catalyst surface during reduction is undesirable with respect to bimetallic particle formation. Chlorine has apparently an inhibiting effect on the mobility of Re in the reduction process. The effect of chlorine on the bimetallic formation is, however, limited as compared to the effect of water during reduction. Addition of water enhances the formation of alloyed particles and this might be due to increased rhenium oxide mobility and stripping of chlorine of the support. Direct physical measurements employing combined EDX/STEM do not reveal any significant differences in alloy formation with increasing chlorine content due to the broad distribution of both the size and the composition of the particles. However, by comparing the shape of the composition — size diagrams in Figs. 1 and 3 it can be observed that the particles are somewhat larger and more alloyed when water is added to the reducing gas.

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