On the Problem of Soluble Platinum in Supported Platinum Catalysts Used for Skeletal Reactions of Hydrocarbons

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Three extraction procedures have been tested to determine the concentration of soluble (i.e., most likely ionic) platinum in various reduced model and industrial supported platinum catalysts. Extraction by a mixture of ethylene diamine and 4% acetic acid gave the most satisfactory results. The concentration of soluble Pt depends on the support used and on the Pt precursor. There is no significant difference found in the selectivity in the hexane/hydrogen reactions in the temperature range between 500 and 600 K between the catalysts with and without soluble Pt. It has been found that the presence of a second component (Re, Sn, Ag) has an influence on the concentration of the soluble Pt. © 1987 Academic Press, Inc.

INTRODUCTION

Almost a quarter of a century ago McHenry *et al.* (*1*) reported that after careful reduction some Pt catalysts contained a nonmetallic soluble platinum, i.e., platinum which can be extracted from the catalysts by dilute HF or by acetylacetone. Some papers that appeared shortly thereafter seemed to confirm the conclusions of McHenry *et al.* Later authors used other extraction procedures, such as complexation by SnCl₂ in alcoholic solution (*2*) and dissolution in dilute H₂SO₄ (*3*). Also, the results of a careful analysis of X-ray diffraction data indicated the presence of nonmetallic platinum (*4*). The extraction by acetylacetone originally suggested has been repeated quite recently, and soluble Pt has been found again (*5*). However, the presence of soluble nonmetallic Pt in well-reduced catalysts has been questioned by some other authors, who have claimed that soluble Pt is only present when the reduced catalysts have been exposed to air prior to extraction (*6–9*). Thus there is controversy regarding the presence or absence of soluble Pt. Moreover, even if Pt were indeed present in a soluble, i.e., most likely an ionic form, some questions still cannot be answered. For instance, one may ask whether the extraction by acetylacetone, SnCl₂, KI, dilute acids, etc., is complete for all different potentially present compounds, e.g., chlorides, oxides, and oxychlorides. Also one may enquire whether this form of Pt plays a role (direct or indirect) in the reactions of hydrocarbons. We addressed ourselves to these problems and report here the results of our short study.

EXPERIMENTAL

Catalyst preparation. Catalysts tested in this study were the standard catalyst EUPT1 (6.3% Pt/SiO₂), two commercial Pt catalysts from Ketjen/Cynamid (CK 303, with nominal 0.3% Pt and 1% Cl on Al₂O₃, and CK 433, with nominal 0.3% Pt and 0.3% Re (and 1% Cl) on Al₂O₃), and several "homemade" catalysts. The latter were prepared by a wet impregnation using either the chlorine-free Pt(NH₃)₄(OH)₂ (preparation at pH 9) or H₂PtCl₆, the latter compound dissolved in H₂O or prepared by Pt metal dissolved in aqua regia and the solution brought into contact with the support. Ground Al₂O₃ was added to a well-stirred aqueous solution of the chosen Pt com-
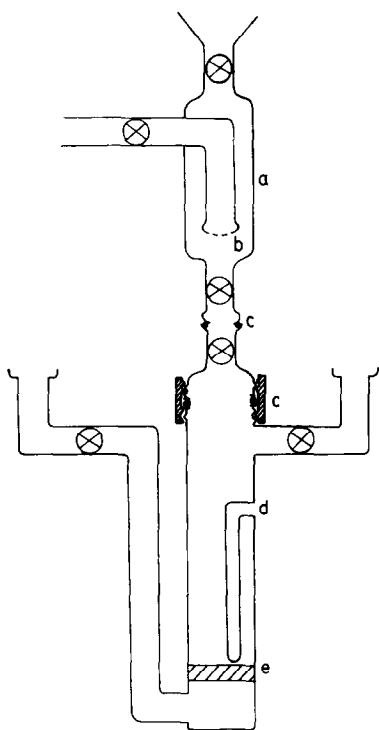
FIG. 1. Flow reactor with extraction setup. a, Reservoir for EDS/HAc; b, inlet for N_2 gas; c, Viton O-ring connection; d, thermocouple well; e, glass filter; $\otimes$, Teflon valve.

pound and stirring was continued for 2–6 h at ambient temperature. Subsequently, and under continued stirring, water was removed by slow heating and evaporation continued up to almost full dryness. The residue was further dried in an oven, at 383 K, for 24 h. Three different Al_2O_3 materials were used, namely, Ketjen/Cynamid γ-Al_2O_3 CK 300, Merck Tonerde γ-Al_2O_3, and Degussa Al_2O_3 Oxid C. For the purpose of comparison a 1% Pt catalyst was prepared from H_2PtCl_6 and silica.

When the catalysts were calcined, calcination was performed in an all-glass flow system in a fixed bed reactor under an air flow of 20 ml/min during 10 h at 623 K. The system was brought to the temperature of calcination or reduction by about 3K min rate of increase. Standard reduction was performed by flow of hydrogen (20 ml/min) at 723 K during 4 h.

Platinum catalysts with a second component (Sn, Re, Ag) were prepared in the same way as the 1% wt Pt catalysts, except in each case 1% wt (i.e., an amount leading to this metal content in the reduced catalyst) of the second component was present. For preparation of Pt–Re catalysts Pt and Re dissolved in aqua regia were used. Pt–Ag catalyst was prepared by impregnating the CK 300 support by Pt in aqua regia and after the slurry was dry an $AgNO_3$ aqueous solution was added and dried again. Pt–Sn catalyst was prepared by impregnating the CK 300 with $SnCl_2$ in acetone, drying, and subsequently adding Pt in aqua regia.

Extraction procedure. The first method we studied was the one described by Bursian *et al.* (2), using a 50% solution of $SnCl_2$ in CH_3OH or C_2H_5OH. The second method was that of McHenry *et al.* (1), employing 2,4-pentanedione (acetylacetone, acac). This extraction was performed under refluxing, during 16 h, whereby the temperature of the solution was increased up to about 400 K. The third method used in this paper was as follows: a solution of 4% acetic acid in ethylenediamine (EDA) was used for the extractions and was applied at 413 K under refluxing during 5–16 h.

Extraction from reduced samples was performed in the *in situ* extraction cell shown in Fig. 1. A cell of this design has also been used in our experiments on Pd catalysts (10). The cell allowed us to use extraction solutions free of oxygen (removed by bubbling through pure nitrogen or hydrogen) and to immerse the samples in extraction solutions in an inert atmosphere. The cell was filled by the extraction liquid and then placed under a reflux cooler and the solution containing the suspension was brought slowly to the desired temperature. In the standard procedure about 1 g catalyst was contacted with 12–15 ml solution and extracted overnight (16 h). While the extraction can be performed easily with exclusion of air, during the further operations (when the catalyst is already covered by the liquids) the surface of the extracting liquid

comes into contact with air (reflux, centrifugation). However, a very low content (≤0.5% Pt ionic/Pt tot) of the soluble Pt determined in some of our catalysts by both the acac and EDA extractions shows that the procedure applied does not itself create appreciable amounts of soluble (ionic) platinum.

Analysis of solutions. In all cases the extract was separated from the solution by centrifugation and the suspension was always carefully washed with hot solutions. The final volume for analysis was 25 ml.

Extracts containing Sn complexes were analyzed by UV/VIS transmission spectrometry.

Extracts obtained by acetylacetone were analyzed by X-ray fluorescence. The apparatus used was a Didac 800 (Intertechnique), equipped with an Ortec 451 spectroscopy amplifier. Am 241 was used as the primary source, Mo as the secondary target, and Li-doped Si as the detector. At least a 7-h counting was used in each determination. According to the calibration line the detection limit was 0.01 mg/ml. Application of atomic absorption spectroscopy (AAS) for analysis of the extracts obtained by acetylacetone appeared to be less convenient since the Al–acetylacetonate complex (probably converted into Al_2O_3) caused troubles upon analysis by blocking the jet of the vaporizer.

Extracts obtained by the third method (EDA) could be analyzed by AAS without trouble. The procedure was as follows. Samples prepared by extraction were compared with calibration solutions, namely, known amounts of Pt (added at H_2PtCl_6) in EDA and 4% CH_3COOH. Such calibration was repeated before each series of measurements. A blank value, subtracted from all data, was obtained by measuring the solution (4% CH_3COOH in EDA) which had been contacted with γ-Al_2O_3 CK 300; the detection limit appeared to be 0.001 mg/ml.

Catalytic test. To check a possible role, either direct or indirect, of the soluble Pt (Pt ions, possibly) in the skeletal reactions of hydrocarbons, a number of catalytic measurements were performed under standard conditions with well chosen representative samples. Catalytic tests were carried out with hexane/hydrogen mixtures (1/17), at total atmospheric pressure and in the low-temperature region (470–630 K). It was assumed that under these conditions the contribution of acidic catalysis is almost negligible. The total flow of gases in the feed was (at 1 bar) 10 ml/min. Analysis of products was performed by GLC. The column used contained 15% squalane on Chromosorb P-AW with dimethylchlorosilane (DMCS; 5 m). The description of the flow apparatus is found in earlier papers (*11, 12*).

One part of the experimental procedure should be specified in more detail. Whatever the procedure, the catalysts always show some decay in activity and the self-poisoning sometimes caused changes in selectivity. Therefore, it is important to choose properly and always follow a certain standard way of comparing various catalysts. With our catalysts, we observed that the decay of activity at the given temperatures is not accompanied by selectivity changes and we adopted the following procedure. Experiments (shown below in Fig. 2) were started at the lowest temperatures and the temperature was increased in steps. After each step, the temperature was kept constant for at least 30 min. When the measurements were performed with a stepwise decreasing temperature (not shown in Fig. 2), starting from the highest temperature, the selectivities for hydrogenolysis and isomerization crossed at slightly higher temperature but the overall picture remained the same (as in Fig. 2).

RESULTS

Determination of Soluble Pt

The first method, extraction by complexation with $SnCl_2$, gives a satisfactory quantitative extraction from various supports of Pt chlorides. However, when Adams-Pt,

TABLE 1

Extractions from the Unreduced 1% wt% Pt/CK 300 Al_2O_3,[a] by $H_2NCH_2CH_2NH_2/CH_3COOH$ Mixtures

Experimental sample preparation	Expected (mg Pt/g cat.)	Determined (mg Pt/g cat.)
1. Impregnated, tested as such	10	10.9
		10.0
2. Impregnated, calcined at 523 K, 5-h reflux	10	9.2
		9.4
3. As step 2, refluxed overnight	10	9.7
		10.0

[a] Impregnation by Pt/aqua regia solution.

consisting mainly of PtO_2, was extracted or when Pt salts on the supports were calcined prior to extraction, extraction was far from being complete. Actually, in the latter cases, only a few percent of Pt was extractable. Therefore, the first method was abandoned in the very early stage of our study and no further research has been done on its suitability.

In contrast to the first method, with the second extraction method (acetylacetone) the Adams-Pt could be dissolved almost completely. Even the thoroughly calcined, not reduced, calibration samples, containing Pt mainly as oxides, allowed almost a quantitative extraction of all Pt out of the sample. Therefore, this method has been studied in more detail than the first one.

When the reduced 1% wt Pt/Al_2O_3 catalysts were extracted and analyzed by the second method, then with the Tonerde and Degussa supports the content of soluble Pt was between 0 and about 3% of the total Pt loading. This was also so in cases when H_2PtCl_6 or Pt in aqua regia solutions were used for impregnation of aluminas. The content of soluble Pt was also rather low (3.5–6.5%) when 2% wt Pt on CK 300 γ-Al_2O_3 catalyst was analyzed, prepared with $Pt(NH_3)_4(OH)_2$ as precursor. In all the cases just mentioned the concentration of soluble Pt was of the same order of magnitude as determined later by the third method (CH_3COOH/EDA), the results of which are described below. However, when the same

carrier (CK 300 γ-Al_2O_3) was impregnated by chlorine-rich solutions, the percentage of soluble Pt became surprisingly high (45–55%). This evoked doubts about the correctness of this method and has actually led us to the introduction of the third method (extraction by CH_3COOH/EDA).

The third method has been tested first with several "calibration" samples. Table 1 shows that extraction is quite satisfactory, even after rather short extraction times, and also from the calcined samples. Extraction was also complete when 1% Pt/SiO_2 was tested. However, it should be noted that the presence of CH_3COOH is essential. Without it the extraction of impregnated uncalcined samples is complete but that of the calcined ones is not.

By the third method, the content of soluble Pt was determined in several catalysts and the results are shown in Table 2. The percentage of soluble Pt is found to be 65 ± 10% for the unreduced industrial catalyst CK 303 sample as such and about 7 and 11% for the reduced CK 303 and CK 433, respectively (these figures depend on the

TABLE 2

Soluble Pt in Model and Commercial Supported Pt Catalysts

Sample	Cl (wt%)	mg Pt/g cat. extracted	
		Dried/reduced	Calcined/reduced
1. 1% Pt/CK 300 ex Pt(NH$_3$)$_4$(OH$_2$)	0	0.08	0.06
2. 1% Pt/CK 300 ex H$_2$PtCl$_6$	1	0.17	0.20
3. 1% Pt/CK 300 ex Pt/aqua regia	1.5	0.32	0.4
4. 1% Pt/Degussa Al$_2$O$_3$ ex Pt/aqua regia	—	0.21	0.21
5. EUPT1 (6.3% Pt/SiO$_2$)	0	—	0.27[a]
6. CK 300 (commercial, 0.3% Pt/CK 300)	1	—	0.18[b]
7. CK 433 (commercial, 0.3% Pt, 0.3% Re/CK 300)	1	—	0.29

Note. The Pt particle size of the catalysts studied fell in the range of 1–2 nm.

[a] Calcined by producers.

[b] After calcination at 523 and 723 K, 1.7 and 1.8 mg Pt/g cat. were extracted, respectively.

TABLE 3

Influence of the Second Catalyst Component on the Amount of Soluble Platinum

	Soluble Pt content (mg Pt/g cat)
Pt catalysts (not calcined) dried at 383 K, reduced at 723 K	
1. 1% Pt/CK 300; ex Pt(NH$_3$)$_4$(OH)$_2$	0.08
2. 1% Pt/CK 300; ex Pt/aqua regia	0.31
Bimetallic catalysts (not calcined)	
3. 1% Pt (ex Pt in air), 1% Re/CK 300	0.1
4. 1% Sn/CK 300	0.07

dryness and the exact Pt content in the given samples).

Inspection of Table 2 reveals that calcination slightly increases the content of soluble Pt in the Cl-containing samples. Furthermore, the high contents of soluble Pt sometimes found by the acetylacetone extraction in the calcined and Cl-containing samples made with CK 300 γ-Al$_2$O$_3$ are not found when the third method is used.

For catalysis by alloys it is interesting to learn whether the concentration of soluble (ionic) Pt in the catalysts after reduction becomes different when Pt salt is codeposited (or coimpregnated) with salts of other metals. One would expect that the concentration of soluble Pt would be higher if the Pt ions were stabilized in the salt or oxide of the second component; on the other hand, the concentration of Pt ions left after reduction would be expected to be lower if the ions of the second component displaced Pt ions from the ion-stabilizing sites in SiO$_2$ or Al$_2$O$_3$. It seemed important to us to investigate the situation in our catalysts. Table 3 shows the results obtained with various samples, after reduction. It appears that the ions of the second component suppress the survival of Pt ions after the standard reduction procedure.

When the Pt–Sn or Pt–Re catalysts are calcined after impregnation, i.e., when "new" ionic Pt is formed by calcination in air which cannot be subsequently displaced from the lattice of the carrier by the ions of

the second component, the amount of soluble Pt in some cases is nearing that of catalysts without the second component. Silver catalysts do not show this type of effect (see Tables 3 and 4).

Catalytic Selectivity

In skeletal reactions with H$_2$/hexane mixture, Pt/Al$_2$O$_3$ catalysts work in industrial reactors under conditions such that (a) a substantial part of the reactions proceeds on the support material while Pt is mainly a dehydrogenating catalyst, and (b) various consecutive reactions occur to an important extent. It is very difficult to prove a possible role for soluble Pt in such a situation (research on this problem is still proceeding in our laboratory). However, at low temperatures the reactions of alkanes proceed mainly on metallic Pt and a possible function (if any is present) of soluble Pt should be better detectable.

Although at low temperatures the acidic function is not expected to be pronounced, we decided to establish experimentally what effect, in principle, could be expected from the acidic centers in γ-Al$_2$O$_3$. The following experiment has been performed. Alumina CK 300 was treated with HCl(g) after reduction and the catalyst was reduced again. After this treatment the Al$_2$O$_3$ contained about the same amount of Cl as the Pt catalyst prepared with aqua regia. Then 1-hexene/H$_2$ (ratio) was led over the catalyst and the product pattern was determined. It appeared that in the whole tem-

TABLE 4

Soluble Platinum Content in the Bimetallic Catalysts, after Calcination at 623 K and Reduction at 723 K

	Dissolved Pt content (mg/g cat)
Pt catalysts	
1. 1% Pt/CK 300; ex Pt(NH$_3$)$_4$(OH)$_2$	0.06
2. 1% Pt/CK 300; ex Pt/aqua regia	0.40
Bimetallic catalysts	
3. 1% Pt, 1% Re/CK 300	0.28
4. 1% Pt, 1% Sn/CK 300	0.29
5. 1% Pt, 1% Ag/CK 300	0.05

perature region used with Pt catalysts, this Pt-free catalyst showed only isomerization. The maximum thermodynamically possible concentration of hexene in the hexane/H_2 reactions is several orders of magnitude lower than the one used in this experiment and thus the acidity-induced isomerization would be of a lower extent than that in the blank experiment. However, the extent is not the main point. It is important to notice that in the range of temperatures applied here there is no acidity-induced hydrogenolysis to be expected with the Pt catalysts containing chlorine.

The variations of the catalytic selectivity with varying content of Pt ions are not very pronounced, as seen in Fig. 2. Figure 2 is representative for the results obtained. The selectivities are presented as functions of temperature in six cases. As in the majority of the published literature (for a review, see Ref. (14)), in the low-temperature region the hydrogenolytic cracking decreases with increasing temperature, while isomerization shows an opposite trend. Calcination bows the curves for hydrogenolytic cracking and isomerization in the direction of higher temperatures so that the two curves, for isomerization and hydrogenolysis selectivities, cross each other at a slightly higher temperature. Variations in the chlorine content and in the percentage of soluble Pt do not lead to a clearly pronounced effect on the selectivity curves in one or the other direction. This is seen in Figs. 2C–F. Experiments have been performed with a number of other catalysts with varying Pt content and with different supports and the same trend as in Figs. 2B–F has always been observed. The results on selectivity are in general quite well reproducible, except with catalysts from $(Pt(NH_3)_4(OH)_2$ as precursor. With these catalysts the total extent of dehydrocyclization varied somewhat irregularly, especially when the catalyst had not been calcined. These catalysts, however, showed the same trend with regard to the hydrogenolysis/isomerization curves as all other catalysts.

DISCUSSION

The first point to be discussed is the question of suitability of various methods for determination of the soluble (i.e., most likely the ionic) platinum. Evidently, the complexation with $SnCl_2$ seems to be of least applicability for determination of ionic Pt. After calcination, most of the Pt is held by oxidic bonds and certainly from some of these complexes Pt cannot be extracted by unassisted extraction using pure $SnCl_2$. The stability of complexes formed by extraction is another point of concern.

It has been shown recently that an exposure of Pd and Pt catalysts to air leads (when the particles of metals are small) to a complete oxidation of the metals (15–17). Therefore, it is not surprising that the chemical methods applied in the presence of air show that a high content of soluble (ionic) Pt is present in the catalysts with the smallest particles (9). But it is not clear to what extent this effect played a role in some of the published data since crucial details of the experiments are not always described (e.g., Ref. (5)).

Our results show that small amounts of ionic Pt can survive a severe reduction. However, the amounts found are of such an order that some less sensitive methods like reflection UV/VIS spectroscopy or the determination of the completeness of the reduction (with the unavoidable problems of the initial Pt valency and spill-over consumption of hydrogen) were not able to determine (or see) them reliably.

In our opinion the results obtained confirm that it is necessary to establish the degree of reduction also by determining the content of the non-zerovalent platinum and not only by measuring the hydrogen consumption. None of the Pt species potentially present (oxides, chlorides, and oxychlorides) can be considered as stoichiometrically well-defined compounds and it is thus difficult to determine that all Pt is present at the start of reduction as, e.g., Pt(IV). However, the determination of
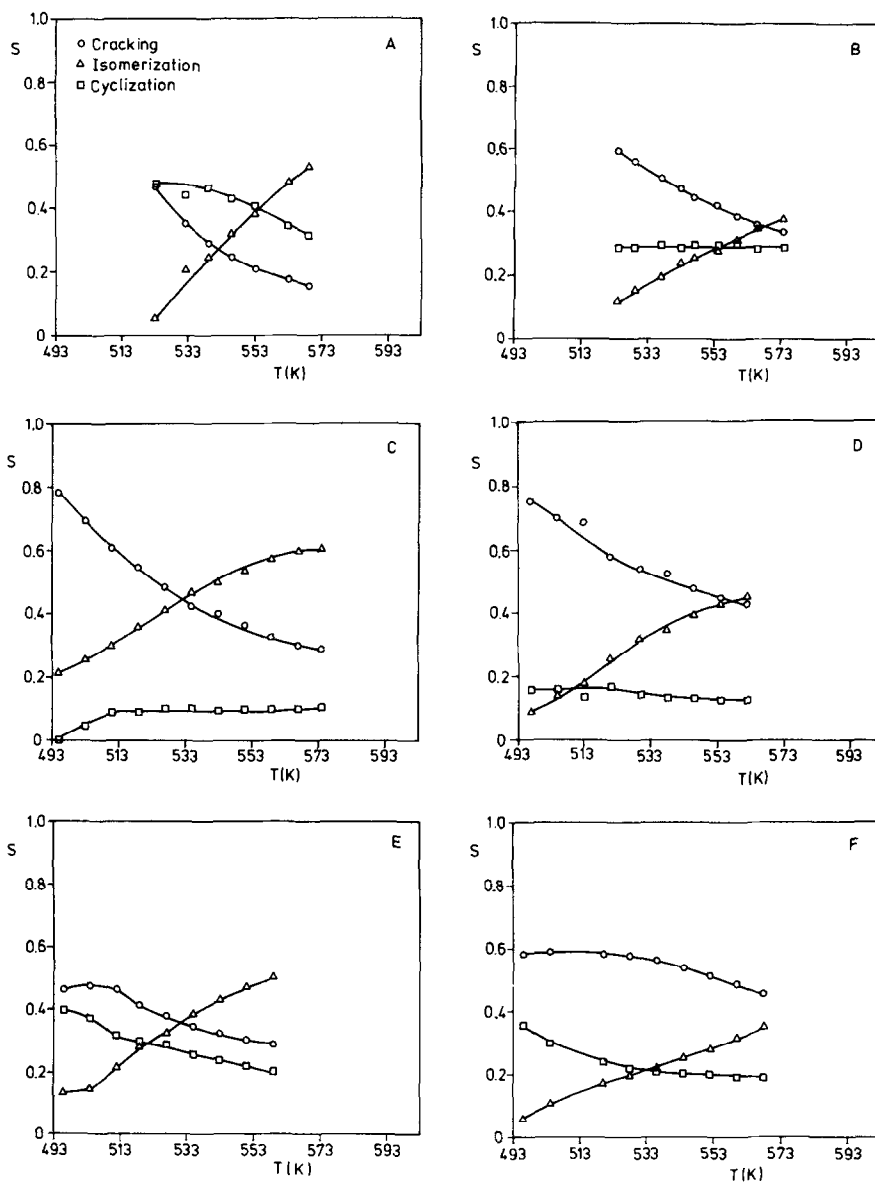
FIG. 2. Selectivity of 1% Pt/Al$_2$O$_3$ catalysts in hexane reactions. Preparation of catalysts was as follows: A, Pt(NH$_3$)$_4$(OH)$_2$, no calcination; B, the same precursor, calcined; C, H$_2$PtCl$_6$, no calcination; D, the same precursor as C, calcined; E, Pt in aqua regia, no calcination; F, as E, but calcined.

the content of non-zerovalent Pt is also not free of difficulties. It is essential to make sure that Pt^0, for example, in a dispersion nearing the atomic one, is not extracted by the ligands used and that Pt^0 is not oxidized during the whole procedure. An indication that this type of artefact is not created by

the procedure applied in this study could be the finding that some catalysts studied, with very small Pt particles, contain almost no extractable (ionic) platinum. For example, one of the 1% Pt/Al$_2$O$_3$ catalysts, that prepared from the Pt(NH$_3$)$_4$(OH)$_2$ complex and calcined at 350°C, has no more than 0.5%

of Pt, as Pt-ions after the standard reduction and extraction.

When we started this study, the extraction by acetylacetone seemed to us to be the most appropriate one from various extractions suggested in the literature. The first experiments revealed that at slightly elevated temperatures of extraction (~350 K) some aluminas dissolved completely (CK 300) and others were at least corroded in the surface layers, and thus Pt ions which are present under the metallic particles (as "anchors") could most likely be reached and extracted. However, with some catalysts, namely, those based on CK 300 and containing excess chlorine, the reaction of acetylacetone with alumina leads to the formation of a dark brown liquid of a high viscosity and X-ray fluorescence showed a very high Pt content in these samples. Later it appeared that even after a long period of standing (some solutions were standing for several weeks before the X-ray fluorescence determination) the viscous dark solution could contain some Pt metal particles, which of course are detected by X-ray fluorescence as soluble Pt. Therefore, the third method employing CH₃COOH/EDA was introduced.

Extraction by CH₃COOH/EDA is satisfactory when calibration samples are used but there is, unfortunately, no independent control available at this moment to reveal whether or not this solution also extracts Pt ions when these are "hidden" in the calcined and reduced catalysts under the metallic particles. It should be noted that the extracts contain some Al, so that the extracting mixture can corrode the surface of alumina. However, in any case the method seems to be reliable in the determination of the presence and quantity of those Pt ions which are accessible to the gas phase or extracting molecules.

Catalytic measurements revealed that differences between various Pt catalysts are indeed observable but in the low-temperature region studied in this paper they are actually not very pronounced. The overall appearance of the selectivity–temperature curves does not change with the method of preparation but nevertheless there are two changes observed. The extent of dehydrocyclization varies and the curves of the selectivities for hydrogenolysis and isomerization acquire a slightly different shape with variations in preparation. With respect to the latter, there is the following to say. All data on different Al₂O₃-supported catalysts (also those not shown in the figures and Tables above) can be subdivided into two groups, namely, those for which the S(isomerization) and S(hydrogenolysis) curves cross in the region around 530 K and those with a cross-point at 550 K or higher. Catalysts of the second group distinguish themselves by the fact that hydrogenolysis persists up to higher temperatures (and isomerization shows up later) than with the catalysts of the first group. The first group if formed by the catalysts which have not been calcined. From these catalysts, the Cl-free catalysts contain almost no Pt ions and those prepared in the presence of Cl contain a small amount of ions. Catalysts belonging to the second group were all calcined. The definitive explanation of the just described shifts is not yet available, and the phenomenon is the subject of further studies.

While the presence or absence of Pt ions does not manifest itself clearly in the hydrocarbon reactions in the low-temperature region, the presence of Pt ions appears to be essential for the syngas (CO/H₂) reactions. Only when Pt ions are detected by the third method of chemical extraction do the catalysts produce some CH₃OH. We will return to this point in another paper. For this paper it is only of relevance that Pt ions, when detected, are (at least a part of them) accessible to the gas phase.

CONCLUSIONS

1. Pt catalysts can contain some unreduced, soluble (most likely ionic) Pt even after a thorough reduction. However,

small-particle Pt catalysts can be also pre-
pared virtually free of soluble Pt.

2. The concentration of Pt ions surviving
the reduction is lower in bimetallic cata-
lysts, indicating that Pt ions can be dis-
placed (during the catalyst preparation)
from the ion-stabilizing sites on the sup-
port.

3. The presence of Pt ions is of rather
marginal influence on the catalytic selectiv-
ity of hydrocarbon skeletal reactions in the
low-temperature region.

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