ature drop over the region is low since little drying takes place due to the low moisture content of the particles and high relative humidity of the gas in this region. Increasing the gas velocity decreases the residence time of the particles in the upper region, thereby decreasing the local conversion and the time for drying, but has relatively little effect on the overall SO₂ conversion.

Conclusions

1. A substantial part of SO₂ conversion takes place in the spray region due to high density of droplets and particles at the constant-rate drying period and due to high turbulence, high droplet surface area, and the droplet flow pattern.
2. Lowering the reactor temperature profile causes competing effects which lead to an optimal temperature for high conversion.
3. The presence of oxygen in the gas mixture does not affect the SO₂ conversion.
4. The CO₂ in the gas mixture competes with SO₂ for reaction with Ca(OH)₂, but the reduction of the SO₂ conversion is only about 5%.

Acknowledgment

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Alumina-Supported Platinum–Rhenium Dehydrogenation Catalysts: Influence of Metal Ratio and Precursors on Catalytic Behavior

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Two series of Pt–Re/Al₂O₃ catalysts with 0.5 wt % loading were prepared by incipient wetness, with the ultimate goal of identifying catalysts that are highly selective for the dehydrogenation of methylcyclohexane to toluene. One series of dehydrogenation catalysts was prepared from H₂PtCl₆ and Re₂O₇ and had nominal Pt/Re atom ratios of 100/0, 75/25, 50/50, and 25/75. The second series of catalysts was prepared from H₂Pt(OH)₆ and Re₂O₇ and had nominal Pt/Re atom ratios of 100/0, 75/25, 50/50, 25/75, and 0/100. These Pt/Re catalysts were characterized by neutron activation analysis, by diffuse reflectance UV spectroscopy, and by model hydrocarbon dehydrogenation and hydrogenolysis activity tests which were conducted in a micropulse reactor. The characterization by diffuse UV/vis reflectance spectroscopy suggests the presence of Re(VI), Re(VII), and Pt(IV) in the freshly prepared and dried catalysts. Neutron activation analysis indicated a significant loss of rhenium after calcination for the catalysts prepared with H₂Pt(OH)₆. In the short-term catalyst screening and activity tests, the use of the chlorine-containing metal salt H₂PtCl₆ measurably increased the hydrogenolysis activity of the resulting catalysts. With respect to the dehydrogenation tests, virtually constant activity was observed on the 50/50, 75/25, and 100/0 Pt/Re catalysts for the conversion of cyclic C₆ hydrocarbons whereas for the dehydrogenation of cyclic C₆ hydrocarbons activity increased continuously with increasing Pt/Re ratio. The unchlorinated 75/25 and 50/50 Pt/Re on alumina catalysts show the most promise for the highly selective dehydrogenation of methylcyclohexane.

Introduction

Hydrogen storage, in the form of liquid hydrocarbons, to be utilized in closed dehydrogenation/hydrogenation cycles has been the subject of continued interest (Taube and Taube, 1981). Such a system based on a methylcyclohexane, toluene, and hydrogen (MTH) cycle has already been tested using commercially available Pt-Re/Al₂O₃ catalysts in the dehydrogenation step (Taube et al., 1983, 1985). However, in the MTH project, hydrogenolysis was clearly a problem given the intrinsic nature of the catalysts and reaction conditions used. Moreover, any level of hydrogenolysis no matter how low will with time exert an accumulative and detrimental effect on the closed dehydrogenation/hydrogenation cycle. Therefore, in the context of supporting the existing project design, specifically improving the selectivity of methylcyclohexane to toluene, catalyst screening and optimization were undertaken with the goal of significantly decreasing the hydrogenolysis rate without decreasing the dehydrogenation activity. As part of this catalyst development, Pt/Re ratios as well as the chlorine introduced by the platinum precursor were the two parameters considered most relevant to study.

It is well-known that the activity and selectivity of bifunctional Pt–Re reforming catalysts depend on the method of preparation (Betizeau et al. 1976a,b; Schay et al.,...
and selectivity tests is available. In this manner, dispersion and selectivity tests using these two series of catalysts. As test hence a rather uniform basis for the analysis of the activity catalysts with nominal Pt/Re atom ratios of 100/0, 75/25, atomic ratios are the remaining parameters to be currently studied. not worthwhile.

Pt-Re catalysts with very low total metal loadings (0.5 wt %) were prepared in the present study in order to guarantee, as far as possible, rather high dispersion in all samples (Wagstaff and Prins, 1979; Eskinazi, 1982). Indeed, if only short-term activity tests are considered, no sintering/deactivation should be expected in these catalysts during the micropulse experiments at 400 °C, and hence a rather uniform basis for the analysis of the activity and selectivity tests is available. In this manner, dispersion is not one of the variables in the present study (at least not as a function of time), and only chlorine content and atomic ratios are the remaining parameters to be currently studied.

In the following, we report results concerning metal loss during the preparation of two series of 0.5% Pt-Re/Al2O3 catalysts with nominal Pt/Re atom ratios of 100/0, 75/25, 50/50, 25/75, and 0/100. One series of catalysts was prepared with Re2O7 and H2PtCl6 (designated chlorinated), and the other series was prepared with Re2O7 and H2Pt(OH)6 (designated unchlorinated). Further, we report the results of the subsequent micropulse activity and selectivity tests using these two series of catalysts. As test reactions, the hydrogenolysis of n-heptane and 2,2-dimethylbutane and the dehydrogenation of methylcyclohexane, cyclohexane, methycyclopentane, and cyclopentane were studied.

Experimental Section

Materials. Degussa-C alumina was used as the carrier for the preparation of both a "chlorinated" and an "un- chlorinated" series of platinum–rhenium catalysts. The Degussa-C sample was used primarily γ-alumina as confirmed by XRD. The BET surface area of the pure carrier, as measured on a Carlo Erba Sorptomat Series 1800 apparatus was 101 m²/g. The approximate bulk averaged chlorine content of the γ-alumina, as quoted by the manufacturer (Degussa), was approximately 0.5 wt %.

The Pt–Re catalysts were prepared from rhenium oxide, Re2O7, hexachloroplatatinic acid, H2PtCl6, and dihydrogen hexahydroxplatinate, H2Pt(OH)6 (Alfa Chemicals). Two different platinum salts were used in order to prepare catalysts with and without added chlorine.

Preparation of Catalysts. All Pt–Re catalysts were prepared with a calculated 0.5 wt % total metal loading. The Pt–Re catalysts were prepared aiming at atom ratios of 100/0, 75/25, 50/50, 25/75, and 0/100 for platinum to rhenium.

The catalyst preparation was by incipient wetness. Ten grams of dry carrier was impregnated with an aqueous solution of the metal salts such that the final calculated metal loading was 0.5 wt %. In the case of solutions containing H2Pt(OH)6, a drop of aqueous ammonia was added to the solution so as to completely dissolve the metal salts. This procedure is equivalent to the use of Pt(NH3)4(OH)2 (Biloen et al., 1980). After coimpregnation, the carrier was shaped into pellets on perforated Teflon sheets and dried at 140 °C for 4 h. The resulting catalyst pellets were then calcined in air at 500 °C for 2 h and then crushed and sieved to a 0.5–1.0-mm mesh.

Concerning the expected oxidation state of rhenium in these catalysts after reduction, it has been suggested that more than 80% of the rhenium in Pt-Re/Al2O3 catalysts is reduced to Re0, even in the case of catalysts prepared with very low total metal loadings (Nacheff et al., 1987). Also, a significant percentage of this rhenium can be assumed to exist in an alloyed state with platinum (Augustine and Sachtler, 1987; Shum et al., 1988).

Catalyst Characterization. Ultraviolet and visible spectra of crushed and sieved catalysts (1.0–0.5 mm) were recorded on a Lambda 9 Perkin-Elmer UV/vis/near-IR spectrophotometer. The diffuse reflectance spectra were collected with a 72-mm integration sphere, using a BaSO4 white standard. Reflectance spectra R(λ) recorded in this manner contain contributions from both the support and the immobilized species. To separate these two factors and isolate the absorption due to the immobilized species, the following procedure was adopted. First, the reflectance R(λ) of the sample was ratioed with respect to the reflectance of the pure support, R0(λ). Second, the Kubelka–Munk function f(R) was calculated according to the standard formula

\[
f(R) = \frac{1 - R/R_0}{2(R/R_0)}
\]

Neutron activation analysis was used to determine the realized metal content of the catalysts after preparation (Atkins and Smales, 1959). Five hundred milligrams of catalyst derived from H2PtCl6 and H2Pt(OH)6, respectively, was subjected to neutron activation analysis after calcination.

Catalytic Tests. The hydrogenation and dehydrogenolysis activity tests of the catalysts with different hydrocarbons were performed in a tubular microreactor (3.1-mm i.d.) which was constructed of type 316 stainless steel and which was situated in the injection block of a Hewlett-Packard Series 5880 autosampling gas chromatograph. A section made up of 1 g of inert glass particles was introduced directly on top of the catalyst particles. The carrier gas was helium/hydrogen (4:1) at a flow rate of 30 mL(STP)/min and a total pressure of 6 bar. Prior to the activity tests, the catalysts were reduced at 400 °C under the helium/hydrogen carrier gas flow (30 mL/min) for 2 h. The injection volumes of the hydrocarbons were 1 µL. Only the first few hydrocarbon injections onto the freshly reduced catalysts showed unrepresentative activity and selectivity patterns. The activity tests were carried out for 24 h with each catalyst. A 10-m capillary column with 23% SP1700 packing was used.

Various examples of the micropulse method for activity and selectivity tests can be found in the literature (Burch and Mitchell, 1984; Menon and Prasad, 1976; Menon and Froment, 1984). In the present study, selectivity (specifically dehydrogenation versus hydrogenolysis) is the single most important issue, and in this regard it has been shown that the selectivities obtained in micropulse reactors (particularly for the dehydrogenation versus dealkylation of methycyclohexane) are similar to those obtained in microcontinuous operation (Newson and Blickenstorfer, 1990). Thus, there is a rather firm basis for using a micropulse reactor for the simple and limited purpose of catalyst screening in the present study, given the rather well defined goal of identifying catalysts that show a minimum of hydrogenolysis activity while maintaining...
Table I. Experimentally Determined Metal Content of Pt-Re Catalysts Derived from H2PtCl6 after Calcination

<table>
<thead>
<tr>
<th>nominal ratio Pt/Re</th>
<th>nominal loading, %</th>
<th>found loading, %</th>
<th>nominal/ found</th>
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<td></td>
<td>Pt</td>
<td>Re</td>
<td>Pt</td>
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<tr>
<td>75/25</td>
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<td>0.13</td>
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<td>50/50</td>
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<td>0.25</td>
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<tr>
<td>25/75</td>
<td>0.13</td>
<td>0.37</td>
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good dehydrogenation activity.

Blank experiments conducted with the microreactor and the glass particles alone did not indicate any significant conversion at the reaction conditions. Cyclohexanol and 3,3-dimethyl-1-butene tests (Pines, 1982) were included in these blank reactions since they are particularly sensitive to the presence of basic and acidic sites, respectively.

For the tests with both the pure support and the Pt-Re catalysts, the microreactor was filled with a 30-mg sample immediately before use. The actual reaction conditions with respect to temperature, pressure, and carrier gas flow rates were the same as in the activation step. The Pt-Re catalysts were investigated with regard to their catalytic behavior using model hydrocarbon activity tests. These tests included the reactions of methylcyclohexane, n-heptane, 2,2-dimethylbutane, cyclopentane, cyclohexane, cyclohexene, and methylcyclopentane.

Conversions and selectivities were defined as follows:

\[
\text{conversion (\%) } = 100(1 - \frac{A_{E,\text{out}}}{A_{E,\text{in}}})
\]  

\[
\text{selectivity (\%) } S_i = 100\left(\frac{A_p}{\sum A_i}\right)
\]

where \(A_{E,\text{in}}\) and \(A_{E,\text{out}}\) correspond to amounts (g) of reactant at reactor inlet and outlet, respectively. \(A_p\) is the amount (g) of product P, and \(\sum A_i\) represents the sum of all products formed from the reactant.

Two tests for surface acidic sites and one test for the presence of surface basic sites were performed. The surface acidity tests were made with the same micropulse system as described above with the use of cyclohexene and 3,3-dimethyl-1-butene as reagents. The activity of the catalysts for cyclohexene isomerization is an indicator for the overall abundance of active sites; 3,3-dimethyl-1-butene isomerized only at sites with strongly acidic character. A 20% (v/v) cyclohexanol in heptane solution was used in the tests for basic sites.

Results

Catalyst Characterization. 1. UV-Vis Spectra. Visually, both the uncalcined and calcined 100% rhenium on alumina catalysts appear white. The catalysts, both uncalcined and calcined, prepared with H2PtCl6 were yellow. The catalysts prepared with H2Pt(OH)6 were yellow before calcination and gray after calcination. The reflection spectra show a strong dependence on the metal deposited; influences of the chlorine content of the platinum precursor as well as changes due to calcination have been detected. The reflectance spectrum of the pure alumina carrier, \(R_{\text{Al}}(\lambda)\), was used as a reference to extract the contribution from the immobilized metal salts to the absorption. The Kubelka-Munk function \(f(R)\) has been calculated, as described in the Experimental Section. The corresponding plots for the uncalcined samples are shown in Figure 1.

2. Neutron Activation. The neutron activation analyses of the uncalcined and calcined Pt-Re catalysts derived from H2PtCl6 and H2Pt(OH)6 precursors revealed a significant loss of rhenium metal after the calcination step for the series of catalyst prepared from H2Pt(OH)6.

Figure 1. (A) Kubelka-Munk \([f(R)]\) plots for spectra of uncalcined 0.5 wt % Pt-Re/Al2O3 catalysts prepared with H2PtCl6. (B) Kubelka-Munk \([f(R)]\) plots for spectra of uncalcined 0.5 wt % Pt-Re/Al2O3 catalysts prepared with H2Pt(OH)6. The abscissa is the photon energy in wavenumbers (1 kK = 1000 cm\(^{-1}\)).

Tables I and II show the metal loading of the "chlorinated" and "unchlorinated" catalysts after calcination.

Catalytic Tests. Pure Support. The isomerization tests with 3,3-dimethyl-1-butane resulted in 77.4% conversion. There was 98% selectivity to 2,3-dimethylbutenes, 1.7% selectivity to 3-methylpentenes, and approximately 0.2% selectivity to 3-methylpentenes. No n-hexenes were observed. Further, activity tests with cyclohexene resulted
Table II. Experimentally Determined Metal Content of Pt-Re Catalysts Derived from H₂Pt(OH)₄ after Calcination

<table>
<thead>
<tr>
<th>nominal ratio Pt/Re</th>
<th>nominal loading, %</th>
<th>found loading, %</th>
<th>nominal found ratio Pt/Re</th>
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<td>25/75</td>
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Figure 2. Conversion of n-heptane and selectivity to toluene as a function of weight % platinum for chlorinated (derived from H₂PtCl₆) and unchlorinated (derived from H₂Pt(OH)₄) platinum–rhenium on alumina catalysts.

in 1.3% conversion. Approximately 13.7% selectivity to methycyclopentane and 50.8% selectivity to methycyclopentene were observed.

In the activity tests with cyclohexanol the selectivities were 98.9% to cyclohexene, 0.8% to methycyclopentene, and 0.3% to methycyclopentane.

The results of the micropulse heptane activity tests are shown in Figure 2. The principle products were either dehydrocyclization to toluene or hydrogenolysis. The activity of the catalysts is roughly proportional to the platinum loading and is considerably enhanced by the addition of chlorine. The selectivity to toluene increases with platinum loading; a maximum in this selectivity is apparent at 75% platinum.

The results of the hydrogenolysis reaction of 2,2-dimethylbutane to neopentane are presented in Figure 3. The platinum-containing catalysts are as expected considerably more active toward hydrogenolysis than the 100% rhenium catalysts, and this activity is enhanced with the use of the chlorine-containing H₂PtCl₆ precursor. The rhenium catalysts show some selectivity to neopentane, however, far less than that exhibited by platinum.

Dehydrogenation: Cyclic C₆ Hydrocarbons. For dehydrogenation activity tests using methycyclohexane as the test reagent, the primary products were toluene, benzene, and cyclohexane. The activity of the catalysts

Figure 3. Conversion of 2,2-dimethylbutane and selectivity to neopentane as a function of weight % platinum for chlorinated (derived from H₂PtCl₆) and unchlorinated (derived from H₂Pt(OH)₄) platinum–rhenium on alumina catalysts.

Figure 4. Conversion of methycyclohexane and selectivity to dealkylated products as a function of weight % platinum for chlorinated (derived from H₂PtCl₆) and unchlorinated (derived from H₂Pt(OH)₄) platinum–rhenium on alumina catalysts.
for conversion to toluene and selectivity to dealkylated products as a function of metal loading are presented in Figure 4. The following points should be noted: (a) the 50%, 75%, and 100% Pt catalysts show virtually identical activity and selectivity patterns; (b) catalysts derived from \( \text{H}_2\text{PtCl}_6 \) are more active than those derived from \( \text{H}_2\text{Pt(OH)}_6 \); and (c) the 100% Re catalyst shows very low activity.

The activity tests with cyclohexane are presented in Figure 5. The principle products were cyclohexene, benzene, methylcyclopentane, and methylcyclopentene. As with the methylcyclohexane tests, the 50%, 75%, and 100% platinum catalysts show essentially identical activity and selectivity patterns. Further, rhenium as expected shows very low activity. The use of \( \text{H}_2\text{PtCl}_6 \) instead of \( \text{H}_2\text{Pt(OH)}_6 \) for the catalyst preparation has only a minor effect.

The principle products observed in the activity tests with cyclohexene were cyclohexene, benzene, methylcyclopentane, and methylcyclopentene. In these tests the presence or absence of platinum is the most important factor. With 0/100 Pt/Re, very low conversion (7%) is obtained with 17% selectivity to \( \text{C}_6 \) ring formation. For the 25%-100% platinum catalysts, conversion jumps to essentially 100% and the selectivity falls to about 2.5%. No significant effect of the choice of the platinum precursor was observed. The presence or absence of platinum is the most important parameter.

Dehydrogenation: Cyclic \( \text{C}_6 \) Hydrocarbons. For activity tests using cyclopentane as the test reagent gave methylcyclopentene as the dehydrogenation product, cyclohexene, cyclohexane, and benzene as the principle ring opening and isomerization products, and hexane as the major hydrogenolysis product. Figure 7 shows that both pure rhenium and pure platinum catalysts have moderate activity. Chlorine added by the platinum precursor \( \text{H}_2\text{PtCl}_6 \) seems to play a less important role than in the cyclopentane tests.

Discussion

Catalyst Characterization. 1. UV-Vis. The alumina support exhibits a highly structured reflectance spectrum. This fact makes it difficult to judge the changes induced by the metal salt impregnations by visual inspection. An interpretation may be attempted with the help of Kubelka-Munk plots (Figure 1), where the reflectance of the pure alumina support is used as the reference \( R_0(\lambda) \) in eq 1. Only wavelength information can be extracted from the Kubelka-Munk representations, and no significance should be attributed to the relative amplitudes of the curves in Figure 1.

The spectrum of the catalyst that was impregnated with \( \text{Re}_2\text{O}_7 \) only is discussed first (top trace in Figure 1A). A high-energy maximum is seen at 30750 cm\(^{-1}\) (325 nm), and a second broad maximum is centered at 19250 cm\(^{-1}\) (520 nm), which may be composed of several peaks. The two maxima observed correlate well with literature data for Re(VII) and Re(VI) oxy anions, respectively. Wang and Hall (1983) have observed prominent absorptions at 240
structures are seen at 33 and 305 nm for rhenium-alumina catalysts, and have attributed them to a species with Re(VI) (Edreva-Kardjieva and Andreev, 1985). Thus it appears that our uncalcined catalyst (100% Re) exhibits prominent bands due to Re(VII) (325 nm) and Re(VI) species (520 nm) on the surface.

With increasing platinum content the high-energy [Re(VI)] absorption is strongly attenuated; two weak structures are seen at 33 500 cm⁻¹ (300 nm) and 26 000 cm⁻¹ (380 nm). The low-energy band continuously shifts to longer wavelengths. For 25% Pt, the maximum is observed at 18 000 cm⁻¹ (555 nm), for 50% Pt the band is centered at 600 nm, and an energy of 15 800 cm⁻¹ (630 nm) is reached at 75% and 100% Pt contents. The low-energy maximum occurs in a region where both the alumina carrier and the catalysts exhibit a smooth decrease in reflectance toward the infrared. The band discussed above shows up when relating the catalyst reflectance R(λ) with respect to the support [R₀(λ)], but not too much weight should be attributed to the shifts of this broad band.

The analysis of the reflectance data for the chlorine-containing catalysts (prepared from H₂PtCl₆ and Re₂O₇; Figure 1B) follows similar lines. As before, two high-energy maxima are seen at 32 500 cm⁻¹ (305 nm) and 26 000 cm⁻¹ (380 nm). The first of these bands is attributed to Re(VI), while the latter might be indicative of Re(IV) (Edreva-Kardjieva and Andreev, 1985) or of Pt(IV) (see below). The long-wavelength absorption exhibits the same shift as observed with the unchlorinated catalysts: the maximum is found at 19 500 cm⁻¹ (515 nm) for 25% Pt, at 19 000 cm⁻¹ (525 nm) for 50% Pt, and at 18 500 cm⁻¹ (540 nm) for 75% and 100% Pt. The observed similarities are not unreasonable since the same rhenium compound (Re₂O₇) was used for both the “chlorinated” and “unchlorinated” series of catalysts.

Finally, the contribution of platinum to the reflectance spectrum will be discussed. For PtCl₆²⁻ in solution, two weak bands are observed at 19 000 and 22 000 cm⁻¹, with stronger bands at 23 000 and 28 400 cm⁻¹ (Cotton and Fackler, 1960). The wavelength of these absorptions shows a strong dependence on the ligand sphere. Thus the gradual changes seen in the low-energy region with varying Pt content are not unreasonable as both Re(VI) and Pt(IV) are contributing to the absorption in this wavelength range.

2. Neutron Activation. The neutron activation analysis indicates that the presence of added chlorine hinders the loss of rhenium from the support. Indeed, the catalysts derived from Re₂O₇ and H₂Pt(OH)₆ show a significant loss of rhenium. These observations are probably related to the known reduction of rhenium to Re⁵⁺, enhanced by the presence of platinum and/or chlorine. This latter aspect has been studied in considerable detail as it relates to Pt/Re alloy formation in Pt-Re/Al₂O₃ catalysts (Mieville, 1984; Malet et al., 1989; Augustine and Sachtler, 1989).

Catalytic Tests. Support. The catalytic tests with cyclohexene and 3,3-dimethyl-1-butene revealed that the Degussa-C support alone exhibits only moderate skeletal isomerization activity in the presence of 1 bar of hydrogen. Specifically, the very low selectivity to 3-methylpentenes, in the tests with 3,3-dimethyl-1-butene, indicates for the most part the presence of only moderately acidic sites. According to Pines (1982), 3-methylpentenes can be formed from 3,3-dimethyl-1-butene on alumina only when the least stable 1⁰ (primary) cation intermediates are involved. By contrast, the tests concerning the isomerization of cyclohexene only confirms that acid sites are present.

Finally, the tests with cyclohexanol suggest that basic surface sites are also present on the Degussa-C sample used in this study. In support of this statement, the high conversion of cyclohexanol and the very high selectivity to cyclohexene are important (Pines, 1982).

Platinum–Rhenium Catalysts. Hydrogenolysis Tests. Since there exist deviations between the nominal and realized rhenium loadings for the Pt-Re/Al₂O₃ catalysts used in this study, but no strong deviations between the nominal and realized platinum loadings, all conversions and selectivities will be reported based on the platinum loadings of the catalysts (wt %).

The conversions of both n-heptane and 2,2-dimethyl-1-butane increased monotonically as a function of increased platinum to rhenium ratio, and also, the conversions were measurably greater for those catalysts prepared with the chlorine-containing platinum salt H₂PtCl₆. This higher observed rate of hydrogenolysis is consistent with (i) the generally higher hydrogenolysis activity observed for platinum than for rhenium (Betizeau et al., 1976a, b) and (ii) the increased hydrogenolysis activity of reforming catalysts with increased chlorine exposure (Menon and Froment, 1984).

Concerning selectivities, the dehydrocyclization of n-heptane to toluene shows a maximum at 75% Pt, for both the H₂Pt(OH)₆/Re₂O₇ and H₂PtCl₆/Re₂O₇ catalysts. This characteristic of platinum–rhenium on alumina catalysts has been noted previously. Betizeau et al. (1976) and Tournayan et al. (1978a, b), starting with H₂PtCl₆ and Re₂O₇ as metal salts, have observed a maximum in the dehydrocyclization of n-heptane at 75/25 Pt/Re for some
2 wt % catalysts carried out under continuous flow. However, this characteristic has also been shown to exist in the platinum–iridium on alumina system by Engels et al. (1984), also carried out under a continuous flow situation.

The selectivity to neopentane in the hydrogenolysis of 2,2-dimethyl-1-butane increased as a function of the platinum to rhenium ratio. This higher selectivity to neopentane observed with platinum catalysts can be rationalized by considering the lower (α-γ) C–C hydrogenolysis rate exhibited for platinum alone as compared to rhenium (Botman et al., 1989).

The "chlorinated" catalysts consistently show a higher hydrogenolysis activity than the "unchlorinated" catalysts in the hydrogenolysis of both n-heptane and 2,2-di-methylbutane. The increased hydrogenolysis activity arises due to both the higher level of chlorination and the higher realized rhenium loadings in these catalysts. Indeed, Re/Al₂O₃ catalysts exhibit slightly higher acidity than the pure support alone (Necheff et al., 1987).

**Dehydrogenation.** The analysis of the dehydrogenation tests can be separated into the behavior seen for cyclic C₅ structures, i.e., methylcyclohexane, cyclohexene, and cyclohexene, and the results obtained for cyclic C₆ structures, i.e., methylcyclopentane and cyclopentene.

There are two identifiable characteristics for the cyclic C₅ tests. For both methylcyclohexane and cyclohexene (i) virtually identical activity patterns and (ii) virtually identical selectivity patterns are seen on 50/50, 75/25, and 100/0 Pt/Re catalysts. The addition of chlorine (H₂PtCl₆) during catalyst preparation seems to be of only marginal importance with respect to the activity of these catalysts.

The *equilibrium* conversions at least for methylcyclohexane at 400 °C in this system are considerably higher than the maximum conversions observed. Additional activity tests with 200 mg of a commercial Pt/alumina catalyst (Johnson Mathey FC50) gave conversions in excess of 90% for methylcyclohexane. Hence, in the above reported activity tests with 30 mg of catalyst (Figures 3 and 4), the observed conversions are sufficiently below the maximum possible conversions under the reaction conditions.

Figures 3 and 4 indicate constant conversion of methylcyclohexane and cyclohexene on the 50/50–100/0 Pt/Re catalysts. Similar behavior has previously been observed by Engels et al. (1984).

With respect to the observed selectivities for hydrogenolysis, specifically dealkylation, it should be mentioned that Grenoble (1979) has studied the dealkylation of toluene on various platinum-group metals. At elevated hydrogen partial pressures, rhenium shows a considerably higher selectivity for dealkylation than platinum. This is consistent with the present results where a much higher selectivity to dealkylation was found for the conversion of methylcyclohexane on the 0/100 Pt/Re catalyst (6% as compared to the 100/0 Pt/Re catalysts with about 0.2% dealkylation). Also the significant rhenium loss measured after calcination for the unchlorinated catalyst may be connected to some extent with the consistently lower selectivity for dealkylation on the catalysts derived from H₂Pt(OH)₄ as compared to those prepared from H₂PtCl₆.

An entirely different behavior with respect to dehydrogenation is seen for the cyclic C₅ structures methylcyclopentane and cyclopentene. That is, the activity of the catalysts is a continuously increasing function of the platinum to rhenium ratio. This has also been noted by Betizeau et al. (1976a,b) and Carter et al. (1982). Chlorination seems to have a consistent and positive influence on the activity, in agreement with the results of Menon and Prasad (1976). Such an effect, increased conversion with respect to both platinum and chlorine content, is consistent with a bifunctional dehydrogenation mechanism (Jossens and Peterson, 1982) forwarded for methylcyclopentane.

**Conclusions**

The present study addressed the problem of identifying catalysts showing very high selectivities for dehydrogenation and very low selectivities for hydrogenolysis, specifically for the reaction of methylcyclohexane to toluene. In this context, it was that for cyclic C₅ hydrocarbons in general, and methylcyclohexane in specific, high activity and selectivity can be achieved in all 50/50–100/0 Pt/Re catalysts tested. Further, the use of chlorinated H₂PtCl₆ or unchlorinated H₂Pt(OH)₄ metal precursors lead only to marginal differences in dealkylation rates in the dehydrogenation of methylcyclohexane for 75/25 and 50/50 Pt-Re/Al₂O₃. However, the difference observed may well be due to the observed loss of rhenium, which alone has a high selectivity for dealkylation. Working under the assumption that the selectivity for the maintenance of the catalysts is a rather clear advantage in the selective dehydrogenation of methylcyclohexane can be seen for the 75/25 and 50/50 Pt-Re/Al₂O₃ catalysts. The only moderately acidic alumina carrier used in this study (Degussa-C) helped to keep the selectivity for hydrogenolysis at a low level and contributed to the low selectivity to dealkylation (0.2%) observed during the dehydrogenation of methylcyclohexane.

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**Registry No.** PtAl₂O₃, 7440-06-4; ReAl₂O₃, 7440-15-5; H₂Pt(OH)₄, 62438-26-3; H₂PtCl₆, 16941-12-1; H(CH₂)₅H, 142-82-5; H₂C₆H₆, 108-88-3; H₂CC(CH₃)₂(CH₃)₂H, 75-83-2; neopentane, 465-82-1; methylcyclohexane, 106-87-2; cyclohexene, 110-82-7; hexane, 110-54-3; cyclopentene, 287-92-3; cyclopentane, 142-82-5; methylcyclopentane, 96-37-7; methylcyclohexane, 27475-50-2.

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Deactivation of Bimodal Nickel Catalyst for Steam Methane Reforming Reaction

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A bimodal nickel catalyst calcined at 873 K (B) showed a rapid deactivation in 160 h in the steam methane reforming reaction at an atmospheric pressure; however, that calcined at 1173 K (N) showed little deactivation in 600 h. The amount of deposited carbon in N was five times as much as that in B. In B the Ni crystallite size was close to the mesopore diameter; however, in N NiAl2O4 was formed and the Ni crystallite was smaller than that. The difference of the deactivations was presumed: a carbon block was formed in a mesopore inside wall near the mouth and an opened area of the mouth was reduced. In B a thicker carbon block with the diameter of the Ni particle was formed and much reduced the opened area to the active mesopore.

1. Introduction

A few activity improvements of catalysts by an application of a bimodal support were reported (Inui et al., 1979; Shimada et al., 1984). The activity improvement is explained by that a macropore keeps an effective diffusion coefficient large and a meso- or micropore wall keeps a surface area for a reaction large (Inui, 1980). Few reports on the life of a bimodal catalyst are reported. A bimodal catalyst for desulfurization and demetalization was only reported to have been available for a long run (Suzuki et al., 1984). In this paper deactivations on bimodal nickel catalysts for the steam methane reforming reaction is reported. The deactivation rate was highly influenced by a difference of a calcining condition between the catalysts after impregnating nickel, which is discussed.

2. Experimental Section

2.1. Catalyst. α-Alumina having a bimodal pore size distribution and a nominal particle size of 5 mm was immersed in an aqueous nickel nitrate solution having a concentration of 4.5 mol/dm3. After being dried at 673 K for 1 h, it was calcined at 873 K for 15 h to provide a catalyst that is referred to hereinafter as B. The catalyst contained 6.8% by weight nickel as measured by induc-