Hydrogenation, Double Bond Isomerization & Aromatization Reactions over Catalysts Derived from Intermetallics & Their Hydrides: A New Route for Catalyst Synthesis

ASHRAF Z KHAN
Department of Chemistry, Jahangirnagar University, Savar, Dhaka Bangladesh

Received 3 October 1986; revised and accepted 15 December 1986

A number of new catalysts has been obtained by redox treatment of ZrCr₂, ZrMo₂, ZrW₂ and their hydrides and their catalytic activity investigated in hydrogenation and double bond isomerization of hexene-1 and aromatization of cyclohexane and n-hexane. The redox temperature and period of treatment exert more influence on the valence state of the Group VIB metals than on the surface compositions of the samples. The activity of the intermetallic hydride catalysts is found to be in good agreement with the transition metal content in intermediate oxidation state. The activities of the hydride catalysts are higher than those of their precursors.

Catalysts containing chromium, molybdenum and tungsten are widely used in petroleum refining industry. The activity and selectivity of such catalysts in hydrogenation and metathesis of olefins and hydrocracking of paraffins depend on the oxidation state of the transition metal. The activity of a catalyst in hydrogenation and double bond isomerization of olefins increases with the decrease in cation valency in good agreement with its reduction ability. However, the supported catalysts, containing the Group VIB metal oxides, are reduced with difficulty. Search is on for newer methods of preparation of Cr-, Mo- and W-containing catalysts, ensuring the formation of intermediate oxidation states of cations. Recent XPS study has revealed that Cr, Mo and W exist in zero and intermediate valence states on the surface of their intermetallics with Zr and the corresponding hydrides. Zirconium existing as selectively oxidative component, prevents complete oxidation of the Group VIB metals.

Presently we have investigated the catalytic behaviour of the intermetallics ZrCr₂, ZrMo₂, ZrW₂ and their hydrides ZrCr₂H₃.₆, ZrMo₂H₁.₈ and ZrW₂H₁.₈ as well as the catalysts derived from the intermetallics and the hydrides towards hexene-1 hydrogenation and double bond isomerization, cyclohexane dehydrogenation and n-hexane dehydrocyclization.

Materials and Methods

The intermetallics of Zr with Cr, Mo and W were always prepared afresh by melting the desired quantities of corresponding metals containing less than 100 ppm impurities under helium atmosphere. The product was remelted 5-6 times in order to obtain uniformity and homogeneity (X-ray diffraction monitoring). Freshly dispersed intermetallic hydrides viz. ZrCr₂H₃.₆, ZrMo₂H₁.₈ and ZrW₂H₁.₈, which were fairly stable at room temperature, were obtained in a specially constructed all-metal vacuum system by direct reaction of the intermetallics with pure hydrogen (generated by decomposition of TiMoHₓ) in the temperature range 470-1270 K and hydrogen pressure in the range 101.3-152.0 kPa (ref. 10). The amount of hydrogen in the hydrides was determined by vacuum thermo-extraction. Samples were given oxidative treatment by heating them in air in a crucible furnace at 673-1073 K for 5 hr. The reductive treatment was given at H₂ flow rate of 2.4 litres/hr at 623 K for 2 hr.

Physicochemical characterization

The specific surface areas of the samples were measured by BET nitrogen and krypton adsorption methods at 77 K. The bulk composition of the samples before or after reaction was checked by X-ray diffraction analysis on a DRON-2 apparatus employing cobalt radiation. The valence states of the Group VIB metals were determined by EPR on a RE-1301 spectrometer. XPS spectra of the samples were recorded with an AEI ES 200B electron spectrometer using AlKα radiation as described earlier.

Catalytic reaction

The catalytic behaviour of catalysts was studied in a hydrogen flow reactor (rate 1.8 litres/hr) fitted with a feed system of splashing (hydrocarbon feed rate 0.5 g/hr) operating under atmospheric pressure. The amounts of catalysts used were varied from 0.3 to 2.0 g with the particle sizes varying from 0.1 to 0.2 mm.
KHAN: CATALYSTS DERIVED FROM INTERMETALLICS & THEIR HYDRIDES

Chromatographically pure (99.9%) hexene-1, n-hexane and cyclohexane were used. The reaction products were analyzed by GLC using a flame ionization detector. A capillary column of length of about 50 nm, containing triethyleneglycol and di-n-butyl ester phase, was used.

Results

Intermetallics

With the exception of ZrCr$_2$, untreated ZrMo$_2$ and ZrW$_2$ were apparently inactive in the hydrocarbon reactions. Only ZrCr$_2$ was active in hexene-1 hydrogenation after hydrogen treatment at temperatures ranging from room temperature to 373 K (Fig. 1a). An appreciable enhancement in activity of ZrCr$_2$ was also observed after oxidative treatment at 673 or 1073 K followed by hydrogen treatment at 623 K (Fig. 1b). The hexene-1 double bond isomerization proceeded in low yield over all the intermetallics. At 573 K the total conversion of hexene-1 decreased drastically. Upon increasing reaction temperature the hexene-1 double bond isomerization over ZrCr$_2$ increased gradually (Fig. 1b). However, both the pretreated ZrMo$_2$ and ZrW$_2$ showed high activity and selectivity (nearly 100%) in the double bond isomerization, particularly the W-containing catalyst at 573-773 K (Fig. 2a).

Intermetallic hydrides

The untreated ZrCr$_2$H$_{3.6}$ was as active as the precursor ZrCr$_2$ in the hexene-1 hydrogenation at 423-573 K, unlike the untreated ZrMo$_2$H$_{0.8}$ and ZrW$_2$H$_{1.8}$. After the redox pretreatment all the intermetallic hydrides showed high activity mainly in the double bond isomerization at 573-723 K (Fig. 2b). The product distribution of hexene-1 over ZrW$_2$H$_{1.8}$ showed that at high conversion the trans/cis hexene-2 ratio was near to equilibrium. The hexene-1 isomerization activity over ZrCr$_2$H$_{5.8}$ and ZrMo$_2$H$_{0.8}$ catalysts was higher than that over the corresponding precursors, unlike ZrW$_2$H$_{1.8}$ which was less active than the precursor ZrW$_2$ (Fig. 2). At temperature > 773 K hydrocarbon destruction with the formation of methane predominated. Increase in the oxidation temperature from 673 to 1073 K in the case of ZrMo$_2$H$_{0.8}$ and ZrW$_2$H$_{1.8}$ resulted in (i) disappearance of n-hexane as the reaction product and (ii) formation of skeletal isomerization product up to 10-20 mass % at 723 K. However, prolonged hydrogen treatment (about 2 hr) of the hydrides oxidized at 1073 K resulted in formation of catalysts whose activity was near to that of the systems oxidized at comparatively low temperature of 673 K, i.e. n-hexane (up to 10 mass % 673 K) appeared again in the products while methylpentenes disappeared.

As already pointed out, there was no difference in the trans/cis hexene-2 ratio for all the intermetallics and their corresponding hydrides. At low conversion
The aromatization of cyclohexane and n-hexane proceeded in appreciable yield over all the intermetallic hydride catalysts at 873-923 K, the Cr-containing catalyst being the most active (Table 1). In contrast, the intermetallics ZrCr₂, ZrMo₂, ZrW₂ as well as well known Al₃Cr₅ after the redox pretreatment were apparently inactive with benzene yield less than 3-5 mass %.

**Discussion**

The hexene-1 hydrogenation over the untreated hydride ZrCr₂H₃.₆ occurred due to hydrogen released from the hydride bulk under the reaction conditions. Hydrogen thermodesorption spectrum of ZrCr₂H₃.₆ showed the presence of an intense peak in the region of 543-573 K (similar to that reported in literature10) and two peaks with low intensity in the region of 413-433 K. Heat treatment of the hydride in the temperature range of 573-623 K, prior to reaction, resulted in the removal of hydrogen from the hydride bulk and consequently loss of catalytic activity. The catalytic activity of ZrCr₂ in this reaction is related to its ability to form hydride at room temperature11, unlike that of ZrMo₂ and ZrW₂. The activity of the untreated ZrMo₂H₀.₈ in hexene-1 hydrogenation was very low, presumably, due to low hydrogen content in its lattice. Moreover, the investigated system absorbed hydrogen irreversibly. In the case of ZrW₂H₁.₈, also inactive in hydrogenation, the dissociation of the hydride with the release of hydrogen was observed at temperature higher than 623 K.

The high activity of all the redox pretreated catalysts mainly in hexene-1 double bond isomerization, is apparently related to the changes caused by redox pretreatment in these systems. XPS studies in an earlier work12 showed that the pretreatment conditions of the Zr-containing intermetallics and their hydrides caused more changes in the valence states of the Group VIB metals than on the surface composition. This implies that surface segregation of the Group VIB metals is not responsible for the higher activity of the investigated systems, unlike the Ni- and Co-containing intermetallic hydrides10.

**Table 1 — Cyclohexane Dehydrogenation over Intermetallic Hydride Catalysts**

<table>
<thead>
<tr>
<th>Catalyst*</th>
<th>Benzene yield, (mass %) at temperature (K)</th>
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<tr>
<td></td>
<td>773</td>
</tr>
<tr>
<td>ZrCr₂H₁.₆</td>
<td>2</td>
</tr>
<tr>
<td>ZrMo₂H₁.₈</td>
<td>6</td>
</tr>
<tr>
<td>ZrW₂H₁.₈</td>
<td>0</td>
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</tbody>
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* Pretreatment in air at 1073 K followed by H₂ at 873 K

**Table 2 — Change in Concentration of Mo(V) Ions in Oxidized Samples under Thermal Vacuum Conditions**

| Sample           | Treatment | g-factor | N, spin/turn over | N, spin/g
<table>
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<tr>
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<tbody>
<tr>
<td>ZrMo₂</td>
<td>723 K</td>
<td>1.927</td>
<td>7.8 × 10¹⁴</td>
<td>1.1 × 10¹⁶</td>
</tr>
<tr>
<td>Do</td>
<td>723 K</td>
<td>1.927</td>
<td>3.7 × 10¹⁵</td>
<td>6.1 × 10¹⁶</td>
</tr>
<tr>
<td>H₂, 723 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrMo₂H₀.₈</td>
<td>Do</td>
<td>1.928</td>
<td>3.5 × 10¹⁵</td>
<td>5.1 × 10¹⁶</td>
</tr>
</tbody>
</table>

* Vacuum 1.3 × 10⁻¹ Pa; * PH₂ = 26.7 kPa

Hydrogen treatment of the oxidized samples at 623 K for 2 hr or more resulted in the appearance of Group VIB metal ions in intermediate or even zero valence states in the surface layer; e.g. Cr(II) Mo(O), Mo(IV), Mo(V) and W(IV). The XPS studies showed that the extent of these components increased with decrease in oxidation temperature and increase in reduction time. The XPS data coupled with catalytic activity of the investigated systems revealed that double bond isomerization of hexene-1, predominant role is played by coordinative unsaturation of the Group VIB metal ions present in the systems. Apparently the difference between the activity of the catalysts derived from the intermetallics and their corresponding hydrides is due to the higher extent of unsaturation in the latter systems. However, ZrW₂ exhibits higher catalytic activity than the hydride ZrW₂H₁.₈ after the redox pretreatment. This may be due to the difference in W(IV) content as well as in the surface composition of the intermetallic and the hydride. The W/Zr ratio in the fresh intermetallic was twice more than that in the hydride. After the redox pretreatment the W(IV) content in ZrW₂ was 2.5 times more than that in ZrW₂H₁.₈. It is worth noting that no appreciable change in the composition of the surface layer and in the valence states of the Group VIB metals was observed in the course of the reactions. It was mainly reductive treatment of the oxidized hydride prior to the reaction which produced appreciable changes in these parameters. However, the specific surface areas of the catalysts derived from ZrMo₂H₀.₈ and ZrW₂H₁.₈ increased with progress of the reaction, unlike that of ZrCr₂H₃.₆ which suffered some decrease.

Apart from this, the EPR results showed an increase in the concentration of the transition metal...
ions with intermediate valence states after hydrogen treatment of the oxidised samples (see Table 2 for the Mo-containing catalyst). In an experiment with nitroxy radical (2, 2, 4, 4-tetramethylpiperidineoxyl) it was established that Mo(V) ions directly participated in the adsorption of radicals and presumably in the catalytic reactions. A strong evidence of participation of the Group VIB metal ions in intermediate oxidation state in catalysis was the absence of catalytic activity of the oxidized but not reduced hydrides upon performing the reaction in helium flow.

X-ray diffraction analysis of the investigated systems revealed that both ZrCr$_2$ and ZrCr$_2$H$_{3.6}$ underwent drastic change in the bulk structure after the oxidative treatment at 1073 K with transformation from crystalline to almost amorphous state. In contrast, oxidized ZrMo$_2$H$_{0.8}$ and ZrW$_2$H$_{1.8}$ appeared amorphous only after being in contact with reductive media — hydrogen, hydrocarbon. The loss of crystallinity resulted in a noticeable increase in the specific surface area and dispersion of the samples (Table 3).

The increase in specific surface areas of the Mo- and W-containing catalysts continued even during the reaction. Presumably, due to this the activity and stability of these catalysts in the hexene-1 isomerization were higher than those of the ZrCrH$_{3.6}$-based catalyst which suffered decrease in surface area.

EPR studies on the oxidised ZrCr$_2$ and ZrCr$_2$H$_{3.6}$ revealed that chromium existed as highly dispersed chromia. The magnitude of the line width in the EPR spectra suggested that the chromia dispersion in the oxidised hydride was higher than that in the intermetallic which exceeded that of the supported Cr$_2$O/ZrO$_2$ catalyst, with Cr:Zr ratio = 2 as in ZrCr$_2$ (Table 4).

All the above mentioned physicochemical characteristics of the presently investigated systems specify their high catalytic activities compared to those of the conventionally prepared supported catalysts. For example, activity/g catalyst of Cr-containing catalysts in the hexene-1 isomerization was of the same order whereas activity/m$^2$ surface area was higher by two orders for ZrCr$_2$H$_{3.6}$ than that for the supported catalyst (Table 5). It should be noted that the monohydride ZrH$_{1.8}$, having only a ZrO$_2$ phase, after the similar redox treatment, exhibited noticeable activity not exceeding 30 mass % in isomerization only at temperature > 673 K.

The results obtained in the present work together with those obtained elsewhere$^{10}$ for intermetallic hydrides containing Group VIII metals, show that the redox pretreatment can serve as a general and an effective method for the preparation of catalysts from the intermetallics and their hydrides for hydrocarbon reactions.

Acknowledgement
The author wishes to express his deep gratitude to Drs V V Lunin and L A Erivanskaya for research facilities and many helpful discussions. The XPS and EPR spectra were recorded at the Zelinsky Institute of Organic Chemistry and Moscow University.

References