2U3UUSUUP 2UUCUՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ ԱՉԳԱՅԻՆ ԱԿԱԴԵՄԻԱ НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ

Հայաստանի քիմիական հանդես 60, №2, 2007 Химический журнал Армении

ON THE MECHANISM ACTIVATION OF HYDROGEN AND HYDROCARBONS ON THE CARBIDES AND HYDRADES OBTAINED BY NON-ISOTERMAL CONDITIONS

P. S. GUKASYAN

Institute of Chemical Physical of NAS of Armenia, Yerevan P.Sevak str. 5/2, Yerevan, RA.

Activation of $ZrNiH_3$ hydride and TiC_x carbides obtained by Self-propagating-High Temperature Synthesis (SHS) method, as well as of natural clinoptilolite was investigated by hydrogen and hydrocarbon in non-isotherm conditions. Positive influence of small quantities of oxygen was observed on activation process. It has been shown that after preliminary activation of carbides and the zeolite surface modified by Cr_2O_3 can be used as substrate in CO hydration process carried out by spillover method in soft conditions. The modified zeolite or activated carbide combined with hydrogen activator, in our case $ZrNiH_3$ hydride, can be efficiently used for rendering harmless the CO toxic gas ejecting into atmosphere, particularly turning it into useful hydrocarbons. The mechanism of hydride and carbide activation, and CO hydration by Spillover method had been discussed.

Introduction

Hazardous carbon monoxide resulting from chemical processes is ejected into environment. The abolition and utilization of even small quantities of this gas is a serious ecological problem. CO is usually oxidized and utilized due to expensive catalytic systems based on noble metals – Pt, Pd, etc. Highly oxidative substances, such as H_2O_2 , are also used for CO oxidation. Along with these the development of new methods and approaches is actual, which could be more efficient for the utilization of this compound. Especially actual are those that are based on the use of less expensive catalysts and are able to carry on the utilization process at less temperatures. It is of great importance for the utilization of this gas to have it converted into valuable compounds – into hydrocarbon and other organic compounds. From this viewpoint the hydration of CO by hydrogen spillover method could be of interest [1,2], which is the main objective of present investigation. By this method, activated hydrogen is formed on solid material surface, which, with surface spillover is taken to corresponding adsorbent and is used as a reaction component. In this case it is necessary to have efficient of CO adsorbents. According to literature data Cr_2O_3 has a quality of this kind. It is precipitated on Armenian natural zeolite, which has a big surface, and the modified zeolite is used as heterogeneous catalyst for CO + H₂ reaction. TiC_{0,6} activated carbide was used as an inert carrier in some experiments.

Experimental

Investigations have been carried out in a reactor of special construction, made for that very purpose, the scheme of which is shown in Fig 1.

The hydrogen participating in hydration is activated in I reaction zone, then it is transferred to II reaction zone, via surface, where it reacts with CO adsorbed on carrier substrate. This is a unique means of bifunctional catalysis, the advantage of which over other catalytic methods is that in this case only one of reagents, the relatively pure one, contacts with catalyst, the other reagents (in our case CO) and the products formed by them do not contact with hydrogen activator, which excludes the toxication of the latter in reactional environment.

As we have already mentioned, the obtaining of active hydrogen should be carried out in the first stage of the process. As hydrogen activator, in our case, ZrNiH₃ hydride obtained by method of self-propagating high temperature synthesis (SHS) at Institute of Chemical Physics NAS Armenia, was used [3].

Results and Discussion

Activation of hydride

The construction of reactor allows obtaining active hydrogen from hydride without pausing the process – in dynamic conditions. Here is how it is realized: a glass-net, on which 1cm thick hydride layer was put, was installed in horizontal section in a 2 cm perimeter Pyrex tube put vertically. The tube-reactor containing hydride was installed in electric stove.



A hydrogen flow of atmospheric pressure was released in ~12 cm³ min⁻¹constant speed through hydride layer and the stove temperature was slowly risen (~10 degrees.min⁻¹). Up to 300 0 C no hydrogen flow change has been encountered. At temperatures higher than that H₂ flow rate self-increase was observed.

If the hydride temperature is kept constant in those conditions, than in ~20 minutes the flow increases, reaches the highest value and again decreases – reaching the previous value. After that no more changes are being encountered. Such hydrogen flow rate change occurs in case of every temperature increase. Increasing and decreasing the hydride temperature many times, it, the hydride, is not only brought to active state, but its activation threshold temperature decrease is observed.



Fig. 2. $ZrNiH_3$ activation threshold temperature dependence from the number of activating experiments: 1 – by pure hydrogen; 2 – 1% oxygen is added to hydrogen.

In our experiments we have succeeded in decreasing it from $300 \, {}^{0}$ C up to $150 \, {}^{0}$ C (see Fig. 2, Curve 1). Hydride properties, activated in that way, are maintained for a long time. This way of hydrogen activation provides a process with stable regime, therefore - reproducible results. Obtained experimental data can be explained in the following way: the activated hydride is in direct and reverse heterogeneous-homogeneous reactions with molecular hydrogen. The balance established among hydrogen amounts having been separated from the hydride and those again joining it are carried out by means of the following reactions:

1. $ZrNiH_3 \leftrightarrow ZrNiH_{(3-x)} + X H_{ads.}$, 2. $X H_{ads.} H_{2gas}$, 3. $ZrNiH_{(3-x)} + H_2 \leftrightarrow ZrNiH_3$,

where X is the hydrogen amount having been separated from one mol of hydride.

Considering the fact, that the presence of the smallest amount of molecular oxygen very often results in heterogeneous catalyst surface state variation, than it was of interest to find out such influence of oxygen on hydride activation process. Experiments showed that if we add only 1% O_2 to hydrogen flow, the activation threshold temperature is established in fewer cases of experiments (see Fig.2, Curve 2). Most probably in the presence of oxygen the decrease in number of activation threshold experiments is conditioned by hydrogen oxidation reactions taking place on the surface. Perhaps in this

case such reactions result in the increase of the number of active centers present on the surface. That process can be presented as follows:

 $\begin{array}{l} \text{4. } ZrNiH_3 + O_2 = ZrNiH_{(3-x)} + HO_{2 \ ads.} \\ \text{5. } HO_{2 \ ads.} + H_{2 \ ads.} = OH \ _{ads.} + H_2O \\ \text{6. } OH_{ads.} + H_2 = H_2O + H_{ads.} \end{array}$

According to reactions mentioned above, in the presence of oxygen, besides H atoms, OH and HO_2 radicals are also formed on the surface, which provide more efficient course of oxygen activation, than is in case of only molecular hydrogen (see Fig.2).

Hydride Surface Microstructure

Considering the fact, that during heterogeneous catalytic processes surface state as well as surface layer morphological changes take place, $ZrNiH_3$ initial and activated states surfaces' microstructures have been thoroughly studied (see Fig.3).



Fig. 3. Not activated (a) and activated (b) ZrNiH₃ hydride surface microstructure.

Investigations have been realized by "BS-300" electronic microscope connected to the computer Pentium III. Fig. 3a and Fig. 3b comparison shows, that in activated state the surface becomes rough, acquires fine porous structure, and covers with fine grind particle formations. Data evaluations presented in figures show, that diameter of particles reaches 3-5 μ m. Investigations have shown that microstructures of samples surfaces activated by pure hydrogen and those by hydrogen-oxygen mixture are the same. These morphological changes of the surface result in surface area increase, which, in its turn, results in reaction rate increase, and is observed in experiment.

Activation of carbide

The TiC, $TiC_{0,8}$ and $TiC_{0,6}$ carbides obtained by the method SHS [4]. Activation this carbides by hydrogen and hydrocarbon with presence of small quantities of oxygen was also implemented by hydride activation method. It has been shown, that $TiC_{0,6}$ carbide is most effectively subjected to activation. X-ray phase analysis of the latter has shown, that activated sample contains not only $TiC_{0,6}$, but Ti_9O_{17} phases as well [5].

The summary activation mechanism of $TiC_{0.6}$ carbide by hydrogen and hydrocarbon may by expressed by reaction

7. $TiC_{0.6} + H_2 + O_2 \rightarrow TiC_{0.6}Ti_9O_{17} + H_2O$ 7'. $TiC_{0.6} + RH + O_2 \rightarrow TiC_{0.6}Ti_9O_{17} + H_2O + CO_2$

Activation and modification of clinoptilolite

In the second stage of the process CO hydration by means of active hydrogen is realized on carriersubstrate. As carrier-substrate, in our case, the RA Novemberyan region clinoptilolite zeolite modified by Cr_2O_3 oxide, was used. The choise of clinopteloit is conditioned by the fact, that with its natural supplies, its purity and qualitative properties, it has productive importance.



Fig.4. a) XRD spectra of the clinoptelolite activated at different conditions 1-300K, P=760 Torr; 2-300K, P=10⁻² Torr. b) \blacktriangle -P=760 Torr and; \bullet -P=10⁻² at different temperatures.

After preliminary cleaning the natural zeolite was ground and fractionated. A 0.02-0.03 cm fraction was used, which, according to literature data [1], is considered optimal for such cases. The X-ray phase analysis has shown, that the raw zeolite used by us contains quite a big amount of water. That is why it was subjected to thermal treatment under $\sim 10^{-2}$ Torr pressure. X-ray phase analysis was carried out by means of Dron-2D diffractometer. Experiments have shown, that depending on treatment conditions, the intensity of the main components' crystalline states existing in the content of zeolite, passes through maximum (see Fig.4).

As we see the crystalline state's quantity of SiO_2 in the range of 250-300 ^{0}C is the biggest. Surface microstructure investigation [6,7] has also been carried out in this range, which shows, that the surface acquires fine porous structure (~1-2 µm). The clinoptilolite having been subjected to such treatment was used as a carrier-substrate, on which the Cr_2O_3 was precipitated. The choice of the latter is conditioned by the fact, that compared to CO it has high adsorption properties, which has significant importance in heterogeneous hydration processes of carbon monoxide. Control experiments have been

carried out for being convinced of it. For that purpose, "Ch. c" marked Cr_2O_3 was ground by vibration mill for 4 hours, particles having ~1 µm size, were obtained. Then the clinoptilolite surface was covered by suspension of that powder. After drying the zeolite, a thin layer of oxide was left on its surface.

Zeolite particles, having been subjected to such treatment, by a 1cm layer were put on the hydride present in the reactor. The hydrogen being filtered through activated hydride provides stable yield of H atoms. The latter get transferred to zeolite surface by means of the spillover, where they react with CO given by a separate tube.

Carbon Monoxide Hydration

Experiments were realized as follows: the molecular hydrogen with the rate of $12 \text{cm}^3 \text{min}^{-1}$, has been given through the lower part of reactor (Fig.1), and CO mixed with He in 5:1 ratio, with the rate of 2 cm³min⁻¹ has been given to clinoptilolite modified by Cr₂O₃, 0.3 cm above hydride layer. Hydration is observed starting from 180 ^oC. Temperature increase results in hydration process rate increase.



Fig. 5. CO hydration kinetics by spillo-ver method: 1 - CO waste, 2 - methane accumulation 1, 2 - The inert carrier is activated and modified clinoptilolite. 1', 2' - The inert carrier is TiC_{0.6}.

Fig. 5 shows the waste of CO and accumulation of methane for two conditions. The results of CO hydration experiments at 230 0 C. In these conditions about 60% of CO turns to methane. In the case when the carrier substance is the activated TiC_{0.6} the CO waste enhanced 62%. The main products of the reaction are CH₄ and H₂O. High hydrocarbons appear in tiny amounts.

Oxygen additions have interesting effect on hydration process. If oxygen, to extent of CO quantities, together with H_2 is given to I zone (Fig.1), than it does not have essential effect on hydration process. But if O_2 is given to II zone together with He + CO mixture, on zeolite surface modified by Cr_2O_3 (Fig.1), than CO hydration decrease is observed. This is a result of the fact, that active hydrogens, which get transferred from I zone to II zone, react also with O_2 , which results in the decrease of their

concentration and therefore in the decrease of CO conversion rate. It can be presented by competing reactions 7 and 8.

8. $CO_{ads.} + H_{ads} \longrightarrow CH_4 + H_2O$ 9. $O_{2ads.} + H_{ads} \longrightarrow H_2O$

It is natural, that in case of O_2 absence the rate of reaction 8 will increase. Therefore, in hydration process CO should be in advance cleaned from oxygen. By special experiments it has been shown, that by using not activated hydride and not modified clinoptilolite, no CO hydration is observed in conditions mentioned above.

К МЕХАНИЗМУ АКТИВАЦИИ ВОДОРОДА И УГЛЕВОДОРОДА На гидридах и карбидах, полученных в неизотермических условиях

П. С. ГУКАСЯН

Изучен процесс активации гидрида $ZrNiH_3$, карбидов TiC_x водородом и углеводородом, а также клиноптилолита в неизотермических условиях. Наблюдалось промотирующее действие следов кислорода на процесс активации. $ZrNiH_3$ и TiC_x синтезированы методом высокотемпературного самораспространяющегося синтеза. Показано, что активированный гидрид или карбид, комбинированный с модифицированным клиноптилолитом, можно успешно использовать для гидрирования СО в мягких условиях. Рассмотрен механизм активации гидрида и карбида водородом и углеводородом, а также гидрирование СО методом спилловера водорода.

ՈՉ ԻՉՈԹԵՐՄ ՊԱՅՄԱՆՆԵՐՈՒՄ ՍՏԱՑՎԱԾ ՀԻԴՐԻԴԻ ԵՎ ԿԱՐԲԻԴՆԵՐԻ ՎՐԱ ՋՐԱԾՆԻ ԵՎ ԱԾԽԱՋՐԱԾԻՆՆԵՐԻ ԱԿՏԻՎԱՑՄԱՆ ՄԵԽԱՆԻՉՄԻ ՄԱՍԻՆ

Պ. Ս. ՂՈՒԿԱՍՅԱՆ

Հետազոտվել է բարձրջերմաստիճանային ինքնատարածման սինտեզի (ԲԻՍ) մեթոդով ստացված ZrNiH₃ հիդրիդի և TiC_x կարբիդների, ինչպես նաև բնական կլինոպտիլոլիտի ջրածնով և ածխաջրածնով ակտիվացումը ոչ իզոթերմ պայմաններում։ Նկատվել է թթվածնի հետքերի դրական ազդեցությունը ակտիվացման գործընթացի վրա։ Յույց է տրվել որ ակտիվացումից հետո հիդրիդը և կարբիդները զուգակցելով ակտիվացված և մոդիֆիկացված ցեոլիթի հետ, էֆեկտիվ կերպով իրականացնում են CO-ի հիդրում մեղմ պայմաններում։ Քննարկվել է հիդրիդի և կարբիդի վրա ջրածնի ակտիվացման և CO-ի հիդրման ժամանակ ածխաջրածնի առաջացման մեխանիզմը։

References

- [1] Poladyan E.A., Gukasyan P.S., Nalbandyan A.B.// DAN USSR, 1984, v.274, №6, p.1417.
- [2] Gukasyan P.S., Mantashyan A.A.// Chem.J.Arm., 1996, v.49, No4, p.81.
- [3] Akopyan A.G., Dolukhanyan S.K., Merzhanov A.G.// Problems of Technological Burning, Chernogolovka, 1981, v.2, p.35.
- [4] Kharatyan S.L., Sardaryan Yu.S., Sarkisyan A.A., Merzhanov A.G.// J Chem. Phys, 1984, v.3, №11, p.1604.
- [5] Hovannesyan Ts. K., Gukasyan P.S., Nalbandyan A.B.// Arm. Chim. J., 1988, v.41, №1-2, p.50.
- [6] Gukasyan P.S., Grigoryan G.L.// Investigation of clinoptilolite's surface modified by Cr₂O₃ used in CO hydration process by means of electronic microscope; The 11th Conferece of AEMS, Yerevan, November 20-21, 2003, p.58.
- [7] Gukasyan P.S., Grigoryan G.L.// Information Technologies and Management, 2006, №1, p.130.