Pore structure of bulk tungsten carbide powder catalysts

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Received 18 November 1994; accepted 31 March 1995

Bulk tungsten carbide catalysts are prepared by direct carburization/reduction of tungsten trioxide in methane–hydrogen mixtures. The catalytic properties of such catalysts have been studied by several authors. The porous structure of these catalysts is studied by adsorption of N_2, Kr, CF_4 and neohexane. Adsorption isotherms and hysteresis loops for the catalysts suggest the presence of a microporous structure made of parallel plates distant approximately by 20 Å. These results are compared to those obtained using such catalysts for hydrogen oxidation and where condensation in the porous structure was observed.

Keywords: tungsten carbide; porous structure; microporosity; hydrogen oxidation

1. Introduction

Since the pioneering work of Levy and Boudart [1] showing the activity of tungsten carbide for neopentane transformation, many teams have studied the potentiality of carbides and nitrides of transition elements as substitute for the expensive platinum group metals. A recent review illustrates the wide range of studies of these materials including hydrodenitrogenation [2], alcohol dehydration [3] and reforming reactions [4,5]. To these, one can also add CO hydrogenation [6] reactions and dihydrogen oxidation [7] and electrooxidation [8].

To become a useful industrial catalyst, this one has to exhibit a sufficiently high surface area, that is at least of a few square meters per gram for bulk powders. Both Boudart et al. [9–11] and Frennet et al. [12] have used tungsten trioxide as precursor for bulk tungsten carbide catalysts and methane–hydrogen (usually 20%–80%) as carburizing mixture. Typically specific surface areas between 10 and 15 m^2/g were obtained by this method, nevertheless samples ranging from 5 to 30 m^2/g can be found in the literature. Such a wide range of specific surface area

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could result from differences in the pore structure of the samples. However, no such information is supplied by the authors of these works.

A good knowledge of the porous structure of catalytic materials is of prime importance, particularly when microporous structures may be involved, as this structure may induce diffusion limitations, thus modifying the overall activity and eventually the selectivity of the catalyst. We have therefore focused our attention on the porous structure, as determined by adsorption measurements, of bulk tungsten carbides prepared by direct carburization of tungsten trioxide.

2. Experimental

2.1. CATALYST

The preparation of the bulk tungsten carbide catalyst (called FB) has been described in detail elsewhere [12]. Let us recall that the starting material was WO_3 (puriss. 99.9% Fluka) which was carburized in a flowing mixture of methane (20 mol%) and hydrogen (80 mol%) at total atmospheric pressure. The temperature was increased linearly from 273 to 1073 K (50 K/h) and maintained at this temperature for 10 h. It was then cooled to room temperature in the same mixture and passivated in a flowing mixture of 2% O_2 in N_2.

Mass balance calculations of the carbon consumption lead to a stoichiometry of $WC_{1.25}$, which is very close to the one determined by elemental analysis ($WC_{1.25}O_{0.03}$, CNRS Vernaison France).

2.2. ADSORPTION MEASUREMENTS

Two series of adsorption measurements were performed using two different apparatuses.

The first one was built of commercial, UHV type, stainless steel elements connected through 2 3/4 Conflat flanges, with the exception of the quartz reactor and of the copper and viton seals. The residual pressure obtained in this apparatus through a Variant VacIon ion pump was in the range of 10^{-8} Torr as measured by a Bayard–Alpert ion gauge. For adsorption measurements, the pressure was measured by a capacitance membrane micro manometer (Barocel from Datametrics) within the range of 10^{-4}–10 Torr. The gases used on this apparatus were: krypton N4.0 (BOC), and CF_4 N2.7 (DuPont FREON-14). Measurements were made at 77 K using liquid nitrogen as isothermal bath, and, in one case, at 87.5 K using liquid argon.

The second apparatus was made of stainless steel tubing (∅ 1/4 inch), Swagelock Connectors and Nupro valves. The reactor containing the sample was made of quartz and connected to the apparatus by the means of Cajon fittings. The pressure was measured using two capacitance micro manometers (Baratron 127A

from MKS), one ranging from 10^{-3} to 10 Torr, the other from 10^{-1} to 10^{3} Torr. Gases used were nitrogen N5.5 (Ucar) at 77 K and neohexane 99% (Fluka) at 273 K.

In both cases the measurement of the isotherms was based on successive expansions of the gas phase from/in known volumes either in the adsorption or in the desorption mode. The latter mode was used in order to measure the eventual hysteresis loop caused by the porous structure of the sample.

3. Results

As suggested by the high carbon to tungsten ratio of the initial catalyst (W/C = 1.25) and shown by ESCA measurements [12], this one is covered by an important excess of carbon. A first round of adsorption measurements was made on this catalyst using krypton at 77 K. The isotherm in fig. 1 shows a step-like behaviour characteristic of the adsorption of this molecule on graphitic surfaces [13]. To confirm this, a second isotherm was measured on this sample at 87.5 K (liquid argon) and an isosteric analysis was made. The variation of heat of adsorption with coverage is shown in fig. 2. The specific surface area calculated using this isotherm is 12 m^2/g for a cross-sectional area of 16 $Å^2$.

After removal of the excess carbon by an ex situ treatment in flowing hydrogen at 1073 K, another Kr isotherm was measured resulting in fig. 3. It appears from this figure that the behaviour characteristic of the adsorption on carbon has disappeared. The resulting isotherm is of type I according to the BET classification [14], that is of the adsorption of a surface contained in a microporous structure.

To estimate the contribution of the microporous surface to the total surface, the adsorption of a larger but nevertheless spherical molecule (CF_4) was measured. It can be seen from curve b in fig. 3 that the shape of the isotherm is of type II of

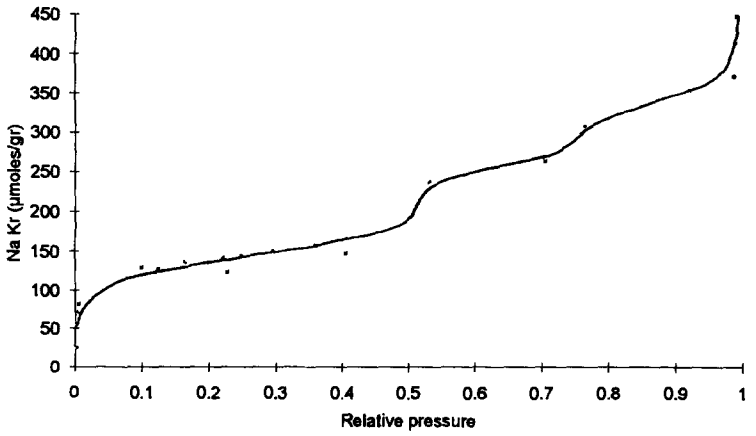

Fig. 1. Kr adsorption isotherm on catalyst FB (no pretreatment).

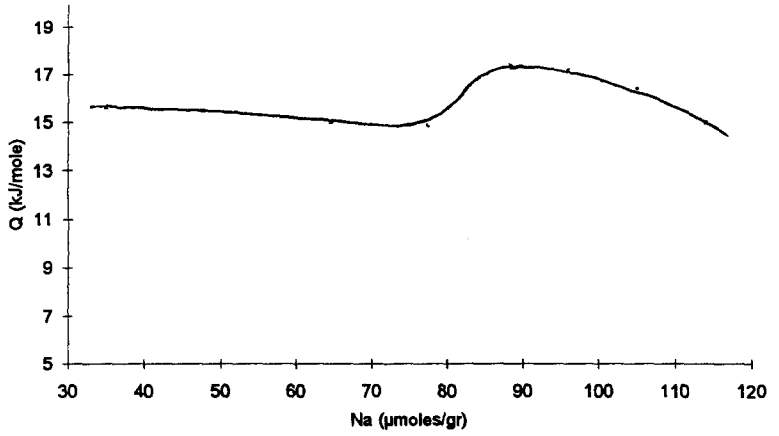

Fig. 2. Heat of Kr adsorption on catalysts FB (no pretreatment).

the classification. That is the shape of a non-porous material. The specific surface are of the catalysts as measured using CF_4 is estimated about 4 m^2/g. This value is certainly overestimated as it is obtained considering a cross-sectional area of 27 $Å^2$/mol, which is certainly excessive. Considering the equation proposed in ref. [15] cross-sectional areas of CF_4 in the range of 19–29 $Å^2$/mol are obtained for densities of ~ 2 to ~ 1 g/cm^3. Even though a density value of 2 would be more realistic in our case, we have chosen a cross-sectional area value of 27 $Å^2$/mol as it will yield a maximal specific surface area for the catalyst. A lower value of this specific surface area as measured by CF_4, would only support the discussion about the porous structure of such catalysts.

During the second round of measurements, a sample of FB catalyst, free of excess surface carbon, was submitted to measurements of nitrogen and neohexane

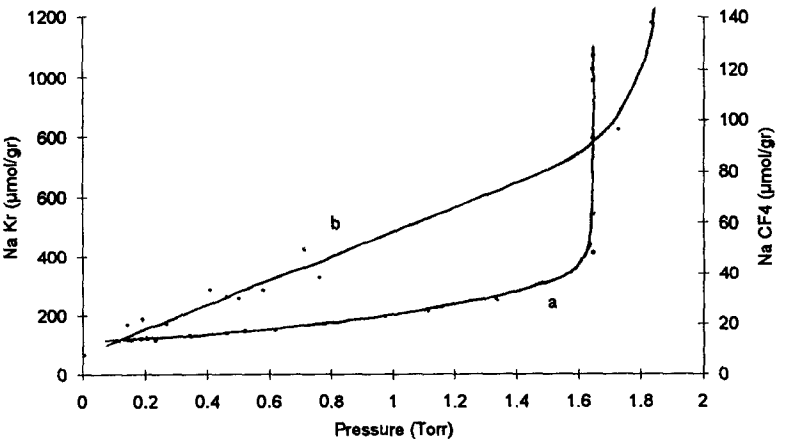

Fig. 3. Kr (a) and CF_4 (b) adsorption isotherms on catalyst FB after excess carbon removal.

adsorption (figs. 4, 5). In both cases, the shapes of the isotherm correspond to the type II, corresponding to non-porous materials. However, an hysteresis loop is observed showing that a capillary condensation phenomenon occurs.

The BET surface area determined using nitrogen is 12.4 m^2/g. For neohexane, preliminary measurements were made on a well-characterised silica support (Aerosil 200 from Degussa) in order to determine the cross-sectional area of this molecule. Using the value of 65 $Å^2$ obtained on the silica support, the specific surface are of the carbide can be estimated to be 14.6 m^2/g.

Table 1 summarises the results obtained on the WC samples after excess carbon removal.

4. Discussion

One can see a good agreement between the values of specific surface are as measured by Kr, N_2 and neohexane. Only this last molecule gives a slightly higher value but is nevertheless in a reasonable range considering in particular that no other references of efficient cross section were found for neohexane other than the one determined experimentally on the silica support.

Only CF_4 yielded a much smaller value of the surface area. As mentioned above, this could be due to an important contribution of a microporous structure to the total surface area. On the other hand, neohexane, which is an even larger molecule than CF_4, seems to be able to reach the entire surface including the one contained in eventual micropores. To understand this, one has to keep in mind that CF_4 measurements were performed at 77 K whereas neohexane adsorption occurred at 273 K. The lower mobility of CF_4 could explain that, after a rapid adsorption on the free surface, the porous structure would be blocked for further adsorption.

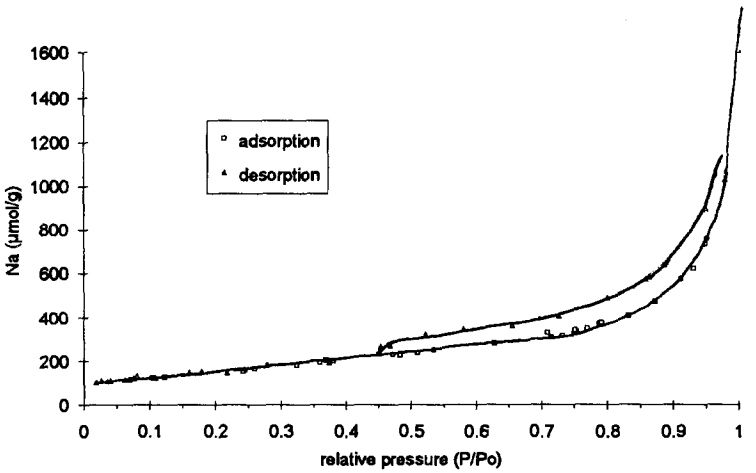

Fig. 4. Nitrogen adsorption isotherm (77 K) on catalyst FB (after excess carbon removal).

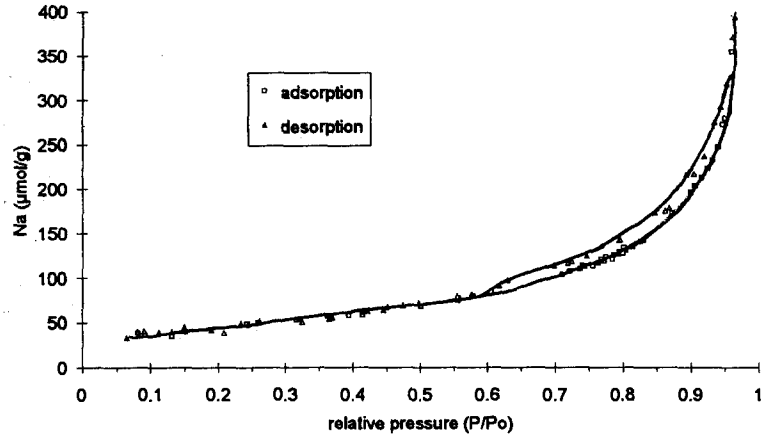

Fig. 5. Neohexane adsorption isotherm (273 K) on FB catalyst (after excess carbon removal).

When considering the shape of the N_2 and neohexane adsorption isotherms, one sees that they resemble those proposed by Gregg and Sing for materials presenting a particular porous structure that is made of parallel plates [16].

The pore size distribution for the tungsten carbide catalyst has been calculated using the procedure of Pierce as modified by Orr and Dalla Valle and is shown in fig. 6. This procedure could be applied only to nitrogen as essential parameters for neohexane are not available. This figure shows an important contribution of pores of less than 20 Å to the total pore volume. The interpretation of this information is delicate as one has to remember that in the case of cylindrical pores the "size" mentioned corresponds to the Kelvin radius of the pores, which would mean pores of a diameter of about 40 Å. Such pores would be considered as mesopores. However, in the case of parallel plates this dimension corresponds to the actual distance between the planes and can, in this case, be considered as micropores.

Recent work [17] has shown that the process of carburization of bulk WO_3 into WC takes place in different steps when a methane–hydrogen mixture is used. First, the solid is reduced by hydrogen into WO_2 (as determined by mass balance). During the second step the interaction of CH_4 with the solid begins. Methane contributes partly to the reduction, along with H_2, and partly to the carburization leading to WC. During these processes the solid is transformed from an orthorhombic struc-

Table 1
Adsorption of Kr, CF_4, N_2, neohexane on WC catalysts after excess carbon removal

	Kr (77 K)	CF_4 (77 K)	N_2 (77 K)	C_6H_{14} (273 K)
monolayer content (µmol/g)	120	25	128	37
spec. surf. area (m^2/g)	11.5	4	12.4	14.6
cross sect. area (Å^2/molec.)	16	27	16.2	65
isotherm type	I	II	II	II

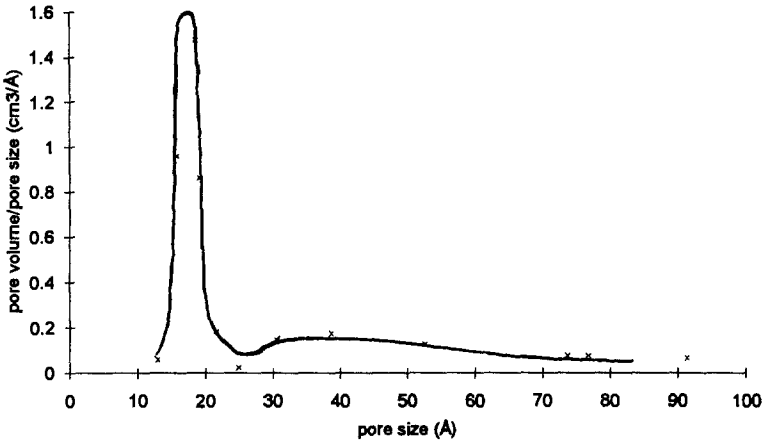

Fig. 6. Pore size distribution determined by nitrogen adsorption.

ture to the final hexagonal structure of WC. As the initial solid has a specific surface are of 3 m^2/g and results in a carbide of 12 m^2/g, this would mean that during the different phase transformations the structure of the solid opens up which could explain the presence of a plate structure as observed by our adsorption measurements.

The importance of this particular porous structure is high when considering these materials for use in catalysis, as it can induce diffusion problems for the reactants and reaction products. To illustrate this point, let us mention the work of Guskey et al. [7]. In this study of the activity of tungsten carbide for hydrogen oxidation, the author observed three different parts in the Arrhenius plot. Below 450 K a constant value of the activation energy was observed; between 450 K and 550 K a higher value of apparent activation energy was obtained, and finally above 550 K the initial value was recovered but with a tenfold higher pre-exponential factor. On the other hand, TPD measurements performed after reaction showed that the water produced by the reaction desorbs in the temperature range of 400–500 K. The authors concluded that below 450 K a large part of the surface is blocked by the water condensation. This meant in other words that below 450 K the activity of the active site was strongly underestimated as the activity of the sample was related to the total surface and not to the accessible surface of the sample. One has to expect such phenomenon to occur when studying reactions at low temperature or when using highly condensable molecules. They should be kept in mind when interpreting kinetic results. If not, the real specific activity of the active site could be strongly underestimated and would thus undermine the real potentiality of such materials as substitutes for platinum catalyst.

5. Conclusion

This work has shown the complexity of the porous structure of tungsten carbide

catalysts prepared by direct carburization of WO_3 in a methane–hydrogen mixture. The presence of such a microporous structure seems to be confirmed by the CF_4 measurement which results in a threefold lower specific surface area, suggesting that this molecule cannot penetrate the narrow pores, especially at low temperature at which the mobility of the molecules is strongly reduced.

The porous structure seems to be constituted of parallel plates distant by 20 Å as the isotherm and hysteresis loop suggest. Such a structure would result from the breaking up of the precursors (WO_3) structure.

It seems of prime importance to keep in mind the presence of such a porous structure when testing the catalytic activity of these catalysts, as part of the surface could be blocked by condensation of one of the reactants, or reaction products, or could induce diffusion limitations. This would lead to an important underestimation of the real catalytic activity of the catalyst and thus of the potentiality of tungsten carbide catalysts as substitute for the platinum group catalysts.

Acknowledgement

This work was supported by a Stimulation Contract No. ST2J-0467-C(TT) from the European Commission. One of the authors (AL) wishes to express his gratitude towards the "David and Alice Van Buuren" Foundation for his research grant.

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