Catalysis Letters 35 (1995) 65–74

Catalytic activity and XPS surface determination of tungsten carbide for hydrocarbon reforming. Influence of the oxygen

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Received 11 November 1994; accepted 30 June 1995

The influence of oxygen on the catalytic properties of tungsten carbide has been studied for the reforming reaction of 2-methylpentane in a great excess of hydrogen ($P_{H_2}/P_{HC} = 150$). The oxygen surface concentration has been measured by the ratio of the signal area of the O_{1s} and the W_{4f} levels as determined by X-ray photoelectron spectroscopy. Two kinds of processes are observed: cracking and isomerization reactions. The introduction of oxygen at $T = 350°C$ leads to a deep decrease of the cracking reaction kinetics; about two orders of magnitude. The tungsten carbide, strongly selective for cracking reactions in absence of oxygen, becomes very selective for isomer production in the presence of oxygen.

Keywords: tungsten carbide; oxygen; alkane reforming

1. Introduction

It has been known for a long time that carbides and nitrides of transition metals like tungsten and molybdenum exhibit interesting catalytic properties for hydrocarbon reforming. For example, ring enlargement reaction of 1,1,3-trimethylcyclopentane on tungsten carbide films at $T = 350°C$ was observed by Muller and Gault [1] and isomerization of 2,2-dimethylpropane to 2-methylbutane and hydrogen/oxygen reaction at room temperature by Levy and Boudart [2]. As these reactions were specific of platinum catalysts, tungsten was thought as a substitute for the platinum metal group. Other interesting reactions have been observed on transition metal carbides: CO hydrogenation on TaC and TiC [3], on WC and W_2C [4], ethylene hydrogenation on TiC, WC and TaC [5,6], carbon monoxide oxidation on TaC, WC and Mo_2C [7] and ammonia synthesis [8].

However, the activity and the selectivity of these catalysts are very sensitive to their surface composition, and the presence of amorphous carbon and oxygen can deeply reduce the activity and changes the selectivity, as shown by Ribeiro et al. [9]

and Iglesia et al. [10]. Previous results obtained in our laboratory have clearly demonstrated this influence [11,12] and have shown the importance of the chemisorbed state (adsorbed oxygen or oxides) of the oxygen on the surface. However, the amount of oxygen on the catalyst has not been measured and no quantitative experiments about this influence have been performed up to now. In the experiments reported in this paper, the catalytic activity and the selectivity of the tungsten carbide for hydrocarbon reforming, determined by the initial kinetics of production of the corresponding molecules, have been correlated with the atomic ratio O/W measured in situ by X-ray photoelectron spectroscopy.

The results clearly demonstrate the strong reduction of several orders of magnitude of the cracking activity which presents an optimum for some O/W values. The isomer production is less strongly reduced and the corresponding selectivity of the catalyst is enhanced. Moreover, some reactions like isomer formation with a quaternary carbon and ring enlargement can happen in the presence of oxygen only.

2. Experimental

The catalyst sample used for these experiments is a tungsten carbide powder prepared by reduction and carburization of tungsten trioxide WO_3 from Johnson-Mattey. This preparation is performed by a hydrogen (80%)/methane (20%) flux (60 cm^3/min) at $T = 800°C$ during 8 h. The surface area measurement by the classical BET method gives a value of 10–12 m^2/g. Before the transfer into the experimental system, the sample must be passivated by amorphous carbon to avoid strong oxidation during the transfer from the preparation cell to the catalytic and surface measurement equipment. To remove this passivation layer, a hydrogen treatment at atmospheric pressure during half an hour at $T = 800°C$ is performed after introduction into the experimental apparatus [13], which does not change very much the BET surface. The catalyst mass used for these experiments is 250 mg, i.e. 3 m^2 of BET surface area. No CO, H_2 and O_2 chemisorption have been performed on this sample in this experiment. However, chemisorption data have been obtained with another equipment where the same kind of samples were prepared and cleaned. The CO, O_2 and H_2 chemisorptions were performed at room temperature and gave the following data: $\theta_{CO} = 0.60$, $\theta_{H_2} = 0.65$, $\theta_{O_2} = 1.25$. If we assume the number of catalytic sites to be determined by the CO or the H_2 coverage, this gives 1.8×10^{19} atomic sites for the catalytic reaction, assuming 10^{19} atomic sites/m^2 for the catalyst determined by the BET. The number of molecules produced per second, given in figs. 4, 5, and 6, can be easily divided by this hypothetic number of catalytic sites, 1.8×10^{19}, to obtain the TON. The catalyst sample, 250 mg, put on a molybdenum holder can be heated by Joule effect and the temperature is measured by a chromel–alumel thermocouple. This holder is located in an ultrahigh vacuum chamber (10^{-10} mb range) where the XPS spectrum of the tungsten carbide can be obtained by a V.G. system. From the O_{1s} and the W_{4f} level signal area, the atomic ratio O/W is calculated by the classical relationship

$$\frac{O}{W} = \frac{A_O}{A_W} \times \frac{\sigma_W}{\sigma_O} \times \frac{\lambda_W}{\lambda_O},$$

where A_O and A_W are the area of the corresponding levels, λ_W and λ_O the corresponding mean free paths and σ_W and σ_O the ionisation cross sections for the photon-electron process given by Scoffield [14].

For the catalytic experiments, the sample holder is isolated by a special device from the ultrahigh vacuum chamber, in a cell where the catalytic experiments are performed at atmospheric pressure under static conditions and with a hydrogen-pressure/hydrocarbon-pressure ratio of about 150; the reaction temperature $T = 350°C$, for at lower temperature and in the presence of oxygen the catalytic activity is too low. At regular reaction times, the gas phase composition is measured by gas phase chromatography and from the corresponding results the reaction kinetics can be deduced at any reaction time for each molecule produced by the reforming process. For simplicity the kinetics at initial reaction time are chosen. The experiments are performed with 2-methylpentane but some results obtained with methylcyclopentane will also be given. These hydrocarbons are usually chosen, for they allow the determination of the isomerisation mechanism which can happen either by a bond shift or by a cyclic intermediary, which can be produced from a hydrocarbon of at least five carbon atoms.

3. Results

The XPS spectra of the catalyst sample after activation, catalytic experiments and oxygen adsorption are given in the figs. 1, 2, and 3 for the C_{1s}, O_{1s} and W_{4f} levels, respectively. On these figures, each curve labelled a, b, c, d, e and f corresponds to the following treatment: (a) activation energy by hydrogen at $T = 800°C$ during 30 min, (b) oxygen adsorption at a pressure of $P = 50$ mb and at $T = 100°C$, (c) oxygen adsorption at $P = 150$ mb and at $T = 200°C$, (d), (e) and (f), successive catalytic experiments without any surface treatment between each catalytic test. After the activation of the catalyst by hydrogen, amorphous carbon is still present on the surface as shown in fig. 1a, where the C_{1s} peak corresponding to amorphous carbon is clearly visible. This treatment does also not allow the complete removal of the oxygen from the catalyst surface, as shown in fig. 2a, where the O_{1s} signal of the surface is given. This oxygen could come from an incomplete reduction of the tungsten trioxide WO_3 from which the tungsten carbide is prepared, or from surface contamination during the recording of the XPS spectra, by oxygen containing molecules like CO or H_2O from the residual gas of the ultrahigh vacuum equipment. This oxygen is present as adsorbed oxygen and oxides, as shown by the XPS spectra given in fig. 3. This conclusion is deduced from the char-

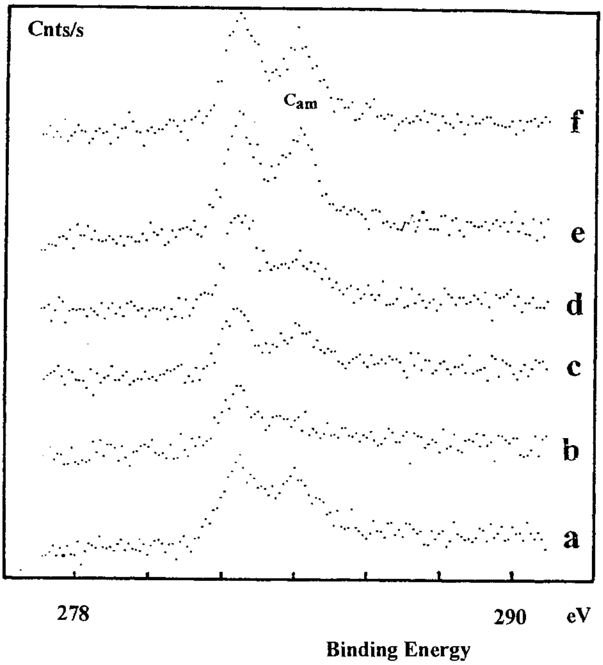

Fig. 1. XPS spectra of the C_{1s} levels. (a) After activation by hydrogen at $T = 800°C$ during 30 min; (b) after oxygen adsorption at $P = 50$ mb and at $T = 100°C$; (c) after oxygen adsorption at $P = 150$ mb and at $T = 200°C$; (d–f) after successive catalytic experiments.

acteristic oxide spectra published in the literature [15,16] and by comparison with the XPS spectra of the passivated tungsten carbide with amorphous carbon where no oxygen is present on the surface. Small contributions of the higher oxides WO_3 and W_2O_5 can also be observed on the surface of this catalyst as shown in fig. 3. By oxygen treatment the amount of these oxides is increased, as shown in fig. 3c. After the successive catalytic experiments, the oxygen quantity on the surface is reduced, as shown in fig. 3, curves d, e, and f, where a decrease of the WO_3 signal can be noticed; the corresponding O_{1s} signal given in fig. 2, curves d, e and f, are also reduced. The decomposition of the W_{4f} signal into several contributions – tungsten carbide, tungsten oxides – can give a crude idea of the surface composition but with a great uncertainty and the corresponding values will not be used here to characterise the catalyst surface. For this purpose, the atomic ratio between the total oxygen atoms present on the surface and the tungsten atoms has been used. This atomic ratio can be easily deduced from the area of the corresponding XPS signals, as previously mentioned.

The catalytic activity is determined by the initial kinetics of formation of the molecules appearing during the reforming process. This process leads to two kinds of reaction, cracking and isomerisation reactions, as already mentioned. Cracking

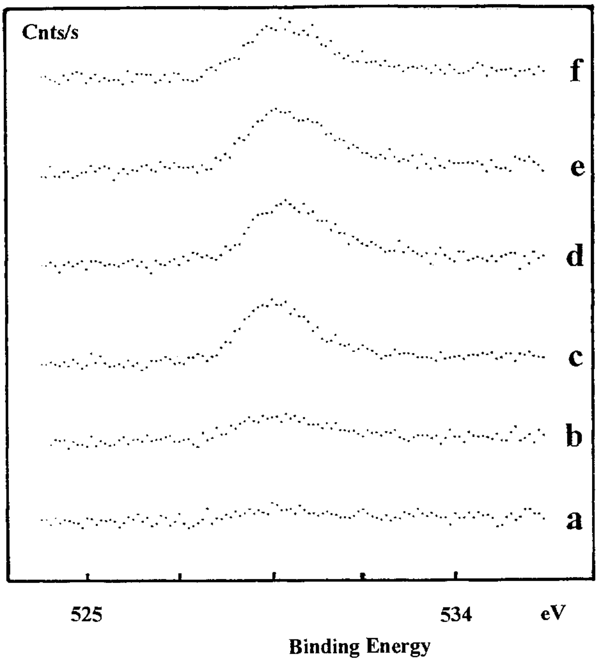

Fig. 2. XPS spectra of the O_{1s} levels. (a) After activation by hydrogen at $T = 800°C$ during 30 min; (b) after oxygen adsorption at $P = 50$ mb and at $T = 100°C$; (c) after oxygen adsorption at $P = 150$ mb and at $T = 200°C$; (d–f) after successive catalytic experiments.

gives methane, ethane, propane, *n*-butane, isobutane, *n*-pentane and isopentane and isomerisation yields 3-methylpentane, 2,3-dimethylbutane, *n*-hexane and 2,2-dimethylbutane. The latter molecules need the presence of oxygen on the surface to be produced [17]. The results are given as a function of the O/W atomic ratio in figs. 4, 5 and 6. For the molecules resulting from the cracking process, the reaction kinetics exhibits a maximum for an atomic ratio of 0.2 except for methane production which decreases continuously, as shown in fig. 4. After this maximum a strong decrease of about two orders of magnitude is observed for an atomic ratio of 0.6. The isomer formation kinetics follow different variations as shown in fig. 6. As already mentioned, at this temperature ($T = 350°C$) no isomer formation is observed on tungsten carbide without oxygen. The kinetics starts from zero for $O/W = 0$ and reaches a maximum value for $O/W = 0.2$, then decreases very slowly except for 3-methylpentane for which this decrease is about one order of magnitude. Some experiments have been performed with methylcyclopentane, for which the ring enlargement reaction, giving cyclohexane and benzene, is only observed when oxygen is adsorbed on the catalyst. The results, which are not reported here, exhibit a maximum at $O/W = 0.4$ for the production kinetics.

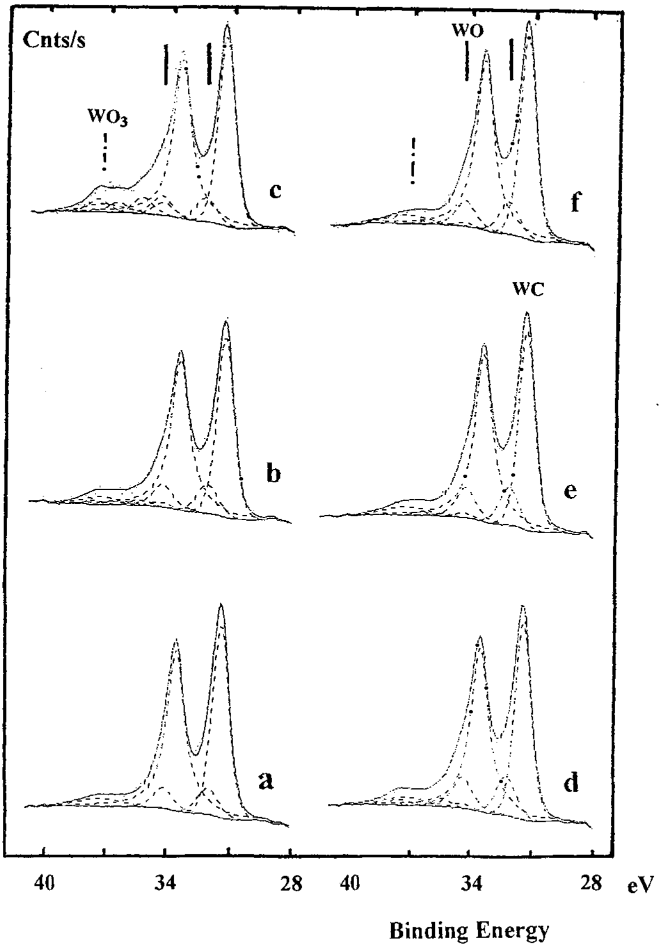

Fig. 3. XPS spectra of the W_{4f} levels. (a) After activation by hydrogen at $T = 800°C$ during 30 min; (b) after oxygen adsorption at $P = 50$ mb and at $T = 100°C$; (c) after oxygen adsorption at $P = 150$ mbar and at $T = 200°C$; (d–f) after successive catalytic experiments.

4. Discussion and conclusions

Comparison with the results obtained on tungsten carbide without oxygen [13], where only cracking reactions leading to methane are observed, shows that the presence of oxygen reduces the cracking kinetics as already mentioned, but it can result in an increase of the kinetics of formation of some molecules. On the clean tungsten carbide surface the kinetics production of the cracked molecules, except methane, obtained by the reforming reaction of 2-methylpentane, *n*-hexane and methylcyclopentane, shows a maximum in function of the reaction temperature. This result can be accounted for by assuming a successive carbon–carbon bond breaking for the cracking process, the number of the carbon–carbon bonds cleaved

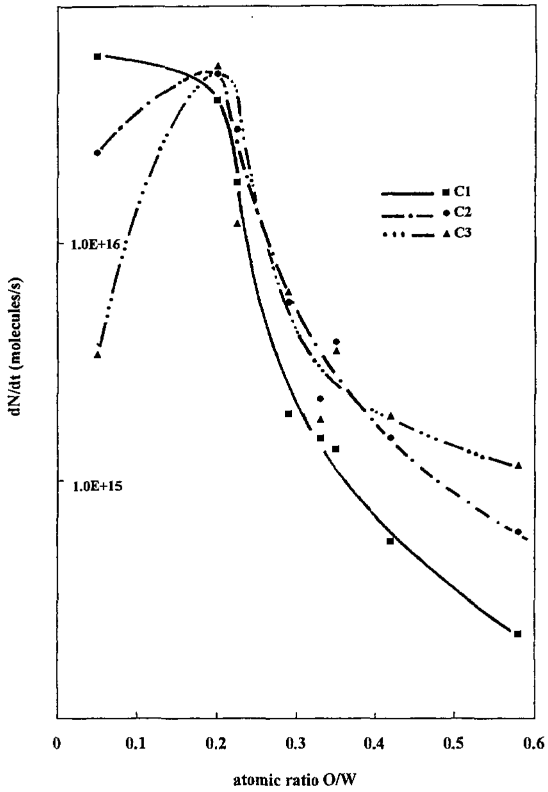

Fig. 4. Formation kinetics of C_1, C_2 and C_3 versus O/W atomic ratio for the 2-methylpentane reforming reaction.

increasing with the temperature. Starting for instance with 2-methylpentane, a single carbon–carbon bond rupture is necessary for *n*-pentane formation. This molecule can undergo another carbon–carbon bond cleavage to give *n*-butane, etc. It is easily understandable that with increasing temperature, the formation kinetics of the molecules first increases, reaches a maximum and then decreases, for at high temperature methane is the only stable molecule. When oxygen is adsorbed on the surface a reverse phenomenon can be observed. Its presence reduces the cracking activity of the surface and at $T = 350°C$, instead of observing methane resulting from breaking of five carbon–carbon bonds of the starting molecule, a lower number of carbon–carbon bonds will be broken and a molecule with a greater number of carbon atoms will become stable. When the amount of oxygen on the surface increases, the cracking properties of the catalyst reach a very low level and no carbon–carbon bonds of the starting molecule can be broken and no cracked molecules are observed. For the skeletal rearrangements of 2-methylpentane and methylcyclopentane, leading respectively to isomers and benzene plus cyclohexane, the kinetic variations with the atomic ratio O/W are slightly different from those for hydrogenolysis reactions. At low atomic ratio O/W (0.2–0.3), a classical bifunc-

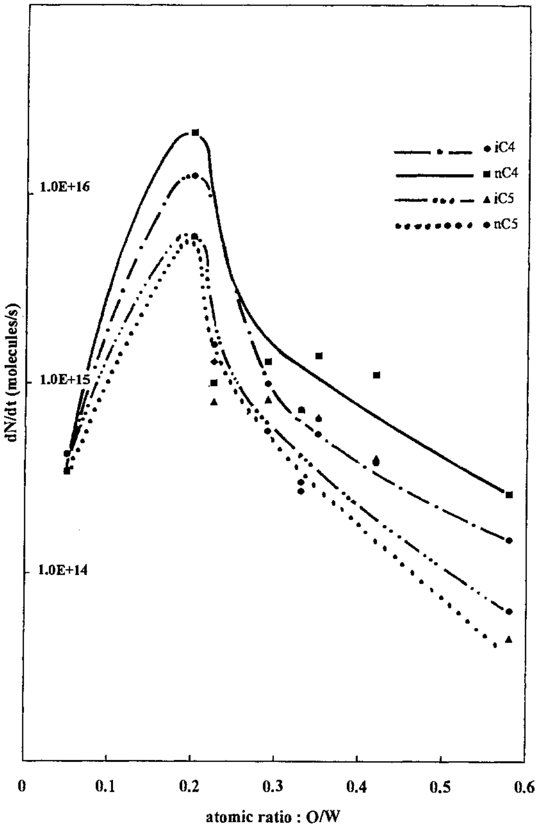

Fig. 5. Formation kinetics of iC_4, nC_4, iC_5 and nC_5 versus O/W atomic ratio for the 2-methylpentane reforming reaction.

tional mechanism takes place. The dehydrogenation/hydrogenation function is attributed to the metallic sites (tungsten or tungsten carbide) and the skeletal rearrangement of the olefins is due to Brønsted acid sites due to the presence of OH groups on the surface [18]. The strengths of the Brønsted acid and that of the neighbouring basic oxygen are important and lead to surface alkoxy species, as already proposed by Cheng et al. [19].

When the atomic ratio O/W increases the activity decreases and the dehydrogenation/hydrogenation function is strongly decreased. The skeletal rearrangements are attributed exclusively to the concerted acidic mechanism via alkoxy intermediates due to the close connection between Brønsted acid sites and the neighbouring basic oxygen, which clearly shows the dual nature of the active sites and that a concerted mechanism takes place as developed recently in refs. [18,20]: carbenium ions are formed from olefins and a carbonium ion is formed from the alkanes. The disappearance of the metallic sites with the increase of the O/W atomic ratio will then explain the existence of the maximum observed in the kinetic curves relative to the skeletal rearrangement reactions.

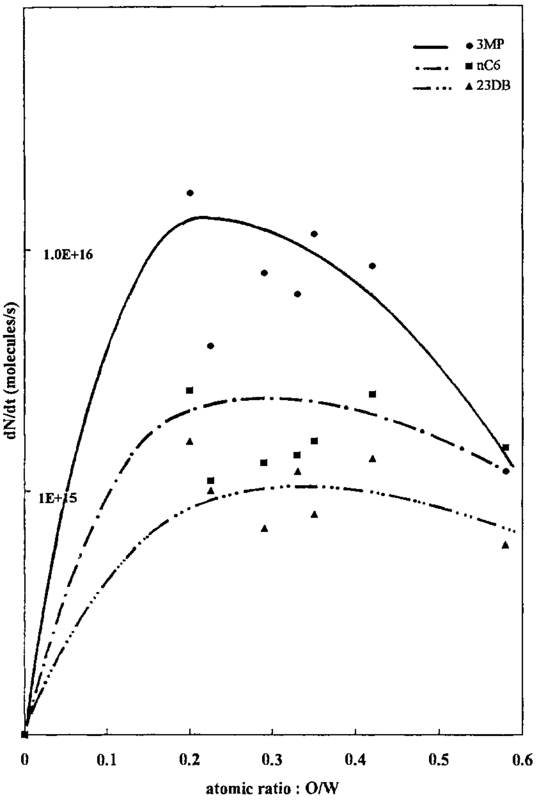

Fig. 6. Formation kinetics of 3MP, nC_6 and 23DB versus O/W atomic ratio for the 2-methylpentane reforming reaction.

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