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REACTIVITY OF TUNGSTEN CARBIDES
I. CATALYTIC AND TEMPERATURE-PROGRAMMED REACTIONS OF METHANOL

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When methanol reacts over tungsten carbide in a steady-state catalytic mode, methyl formate is formed with a selectivity higher than 90%. On the other hand, temperature-programmed decomposition of methanol preadsorbed on the same surface produces mostly carbon monoxide. The difference in selectivity in both modes of reaction is discussed. By contrast, platinum catalyzes the transformation of methanol to dimethyl ether with high selectivity.

Keywords: Tungsten carbide, methanol reactions

1. Introduction

Methanol has received attention in recent C_1 chemistry [1]. Depending on the catalyst [2], methanol goes to methyl formate $HCOOCH_3$ on Cu [3–6], to CO and H_2 on Ni [7] or W [8], or to dimethyl ether CH_3OCH_3 and hydrocarbons on Pt and acid catalysts. With some catalysts, these three reactions take place simultaneously [2]. Minor products often observed in methanol reactions are CO_2, CH_4, and HCHO.

Recently, Miyazaki et al. [9] studied the catalytic methanol reactions over unsupported WC at 473 K and atmospheric pressure in a closed recirculation system and found that $HCOOCH_3$ was formed with a selectivity greater than 90%. The other products were CO and H_2. The authors noted the similar selectivity of WC and Cu. By contrast, in a temperature-programmed decomposition (TPR) of methanol preadsorbed on a single crystal surface W(100) with a (5×1)C overlayer, Ko et al. [10] found CO and CH_4 to be the major products, with only 2% of $HCOOCH_3$ among the carbon containing products. Our objective was to investigate this selectivity pattern for methanol in TPD and catalytic

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modes over the same high surface area βW_2C [11]. Since previous work in our laboratory shows analogies in catalytic behavior between WC and Pt [12,13], we also compared Pt with βW_2C as catalysts for methanol decomposition.

2. Experimental

The unsupported tungsten carbide used in this study is a face-centered cubic structure designated in the literature as βWC_{1-x}. Since x is close to 1/2, we shall call it simply βW_2C. Preparation of this high specific surface area powder is described elsewhere [11]. A sample Pt black (Engelhard) was used as received. A 1 wt% Pt/C catalyst was prepared by incipient wetness impregnation of Spheron 6 (Cabot) with chloroplatinic acid dissolved in ethanol [14]. The sample was then dried at 343 K for 10 h in air.

After preparation, W_2C was transferred to a volumetric adsorption system. Before the adsorption of gases, the sample was treated in flowing Pd-diffused H_2 (Liquid Carbonic) at 573 K for 2 h. The number of presumed active sites on βW_2C was determined by irreversible chemisorption of CO at room temperature (RT), defined as the adsorbed CO that could not be evacuated at RT. One molecule of chemisorbed CO was assumed to titrate one site. The specific surface area S_g was determined by means of the N_2 BET method. The BET area was used to estimate the particle size D_p from the equation $D_p = 6/(\rho S_g)$ where ρ denotes the density of the solid. The sample was then transferred to a catalytic reaction or a TPR system. By performing sample preparation, gas adsorption and reaction in the same cell which could be isolated by two stopcocks, the sample was never exposed to air between these steps. The 1% Pt/C was treated in flowing O_2 at 570 K for 0.5 h, flushed with He (99.995%, Liquid Carbonic), purified by passage for 0.5 h through 5A molecular sieve followed by a MnO/SiO_2 indicator, and then was reduced in flowing H_2 at 703 K for 1 h. The number of exposed platinum atoms was measured by means of a O_2–H_2 titration [15].

The bulk structure of W_2C was determined by powder X-ray diffraction (XRD). Unlike the sample used for the reaction, the sample for XRD was passivated with flowing 1% O_2 in He at RT. The crystal size D_c was estimated from the Scherrer equation (see table 1).

The catalytic methanol reaction was studied in a closed recirculation system similar to that used before [16] and likely to be free of temperature and concentration gradients in the catalyst bed due to small conversion per pass. The powdered sample (about 100 mg) was evenly dispersed on a fritted quartz disc in a reactor, pretreated in flowing H_2 at 470 K for 0.5 h, and then evacuated to 10^{-4} Pa at RT. The reaction mixture contained methanol (Aldrich > 99.9%, HPLC grade) at 3 kPa and He at 98 kPa. The reaction was started when the sample at a desired reaction temperature contacted the circulating reacting mixture.

Temperature-programmed reaction (TPR) of methanol was performed in a flow system. The sample was pretreated as in the catalytic mode. The He saturated at RT with methanol was fed at the rate of 66 μmol s^{-1} over the sample maintained at RT. After 1 h of methanol adsorption, the gas was switched to pure He to flush out gas phase methanol. The TPR was started after 0.5 h of He flushing by heating the sample at the rate of 0.067 Ks^{-1}. In both catalytic reaction and TPR, the products of the reaction were analyzed by on-line gas chromatography (HP 5880) with a thermal conductivity detector. A 1.4 m long, 3.2 mm diameter Poropak T column was used to separate different products.

3. Results

Characterization data for the samples are shown in table 1. The BET surface area S_g of βW_2C was 81 m^2g^{-1}. This corresponds to particle size of ca. 4 nm in good agreement with average crystal size of 4 nm estimated from X-ray line broadening. The powder X-ray diffraction showed only peaks corresponding to a cubic crystal with a lattice parameter of 418 pm, in good agreement with the reported values of 422 pm [17] and 412.5 pm [18] for βW_2C, both prepared at temperatures above 3000 K followed by rapid quenching [17]. Our βW_2C chemisorbed 315 μmol g^{-1} of CO irreversibly at RT. This indicates that 24% of potential surface sites chemisorb CO irreversibly at RT. The number of surface W atoms was estimated from BET area and a W site density of 1.0×10^{15} cm^{-2}. For 1% Pt/C sample, O_2–H_2 titration showed that 12% of total Pt was exposed.

The main products of the catalytic reaction over βW_2C in the closed recirculation system were $HCOOCH_3$ and CO (fig. 1). These two products accounted for more than 99% of consumed methanol. The concentration of $HCOOCH_3$ showed a maximum while that of CO increased gradually throughout the run. The maximum in $HCOOCH_3$ may be due to the decomposition of $HCOOCH_3$ to

Table 1
Characterization of the samples

	βW_2C	1% Pt/C
BET surface area/m^2g^{-1}	81	–
% active sites of total metal (W or PT)	6.0 [a]	12 [b]
Particle size/nm		
D_p by BET [c]	4	–
D_c by X-ray [d]	4	–

[a] By irreversible CO chemisorption at room temperature.

[b] By O_2–H_2 titration [15].

[c] $D_p = 6/(\rho S_g)$, ρ = density of the solid.

[d] $D_c = \lambda/(\beta \cos\theta)$, λ = wavelength of CuK X-ray radiation, θ = Bragg angle, β = halfwidth of diffraction peak corrected for k_α-doublet separation and instrumental broadening.

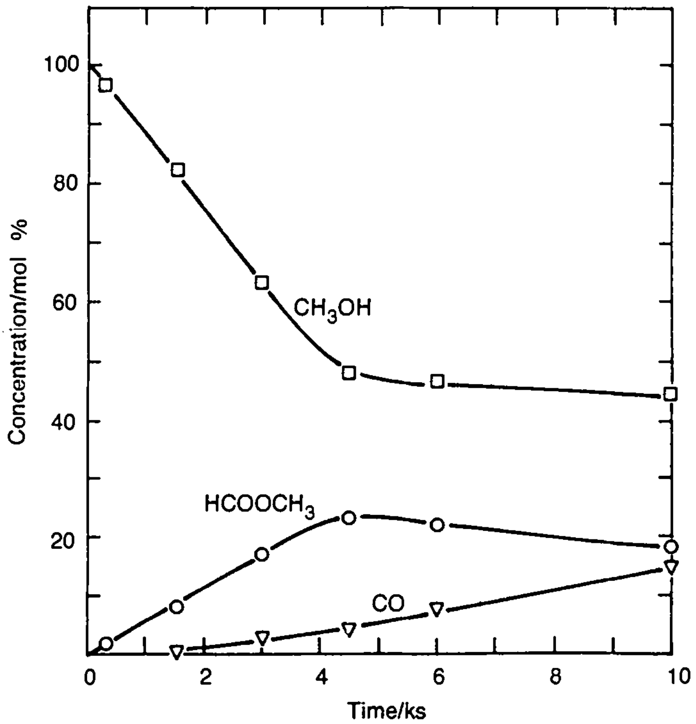

Fig. 1. A typical concentration-time relationship for the catalytic methanol reaction over βW_2C. Temperature: 460 K. Reactant: 3 kPa of methanol (3 kPa) in He (98 kPa). Sample weight: 85 mg.

CH_3OH and CO which has a ΔG° value of ca. -25 kJ mol^{-1} at 460 K [19]. A small amount (less than 1 mol% of the products) of CO_2 and CH_4 was also formed. No HCHO was detected. The formation of HCHO by dehydrogenation of CH_3OH has a positive ΔG° below 720 K [19], and high selectivity for that reaction has been reported only at high temperatures [20]. Dihydrogen was also produced, but the amount was not quantified. An Arrhenius plot gave an apparent activation energy of 134 kJ mol^{-1} for methanol conversion of βW_2C.

The results for the catalytic reaction are summarized in table 2. The data for WC of Miyazaki et al. [9] are also included for comparison. Their WC was a commercial product (Materials Research Co.) and was evacuated at 4×10^{-4} Pa and 1173 K before reaction in an attempt to remove surface oxide. It had a hexagonal crystal structure and specific surface area of 1.3 $m^2 g^{-1}$ [21]. The rate of methanol conversion over our βW_2C was fairly constant (up to ca. 40%) as seen in fig. 1. In addition to turnover rates, rates of the reaction are also expressed as areal rates v_a, defined as the number of methanol molecules converted to products per BET surface area of the catalyst per second. Selectivity S for a product is defined as the % of reached methanol that forms the product. In the case of $HCOOCH_3$, S_F is $100 \times (2 \times$ mol of $HCOOCH_3$ produced/mol of

Table 2
Catalytic methanol reactions at 473 K

Catalyst	S_g [a]$/m^2g^{-1}$	V_a [b]$/10^{13}$ $s^{-1}cm^{-2}$	V_t [c]$/s^{-1}$	S_F [d]	S_E [d]
βW_2C	81	3.5	0.14	95%	0
WC [e]	1.2	1.3	–	90%	0
1% Pt/C	–	–	0.012	0	84%
Pt black	–	–	–	0	55%

[a] BET surface area.

[b] Areal rates defined as the number of methanol molecules converted to products per BET surface area of the catalyst per second.

[c] Turnover rates defined as the number of methanol molecules converted to products per presumed active site (W or Pt) per second.

[d] Selectivity to $HCOOCH_4$ (S_F) and CH_3OCH_3 (S_E) at 20% CH_3OH conversion.

[e] From ref. [9].

CH_3OH reacted), since two molecules of methanol are needed to form one molecule of $HCOOCH_3$.

The areal rate of catalytic methanol reactions over our βW_2C is very close to that for WC [9] as well as selectivity to $HCOOCH_3$ at 20% CH_3OH conversion. For both supported and unsupported Pt catalysts, the major product was CH_3OCH_3, and $HCOOCH_3$ was not detected in the products. The turnover rate for Pt/C was 10 times lower than that for βW_2C.

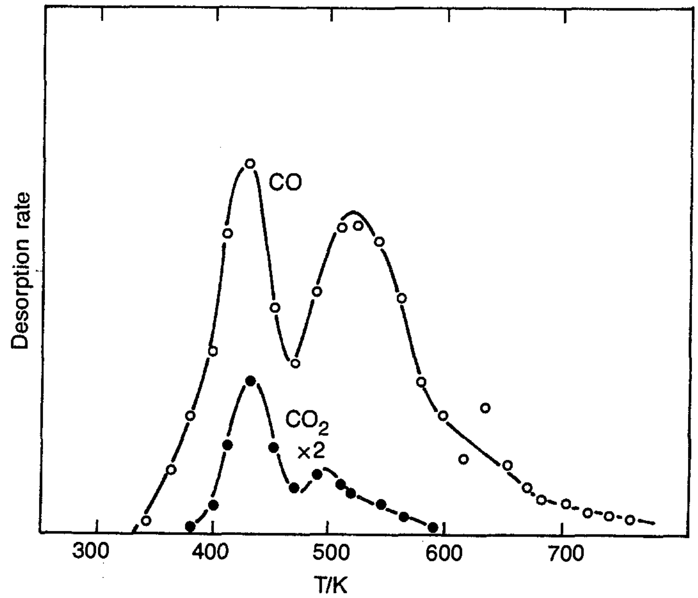

Fig. 2. Temperature programmed reaction of methanol over βW_2C. Methanol was adsorbed at room temperature before heating the sample at the rate of 0.067 Ks^{-1} in He carrier gas flowing at 66 $\mu mol\ s^{-1}$.

The results of temperature-programmed methanol reaction are shown in fig. 2. Sampling was done every 300 s, or at every 20 K increment of temperature. Major products were CO and CO_2. Neither $HCOOCH_3$ nor CH_3OCH_4 was detected.

4. Discussion

Catalytic Reactions

The catalytic methanol reactions over our βW_2C catalyst produce mainly $HCOOCH_4$. This selectivity is very similar to that observed for WC by Miyazaki et al. [9]. Both catalysts also show very similar values of areal rates in spite of differences in crystal structure and specific surface area. Recently Sodesawa et al. [6] studied the same reaction over Cu/SiO_2. The exposed specific copper surface area S_g was titrated with N_2O at 363 K. Areal rates did not change for catalysts with S_g between 50–400 $m^2(g\text{-}Cu)^{-1}$, but decreased about 100-fold as S_g increased from 400 to 1000 $m^2(g\text{-}Cu)^{-1}$. From the latter observation, the authors concluded that the reaction of methanol over Cu is structure sensitive. In terms of particle size $D_p = 6/(\rho S_g)$, where ρ is the density of Cu, the results do not show a particle size effect on the rate between 1.8 and 14.4 nm, but show it between 0.7 and 1.8 nm. Since there is no variation of the areal rate in most of the critical particle size range between 1 and 10 nm where surface structure varies most greatly with particle size [22–24], we think that the reaction is structure insensitive. Reasons other than surface structure could have contributed to the 100-fold variation in areal rate for Cu particles smaller than 1.8 nm.

As mentioned, only copper-based catalysts are known to produce $HCOOCH_3$ with high selectivity. Considering that a W wire produces only CO and H_2 under similar conditions [8], the selectivity to $HCOOCH_3$ observed on tungsten carbides is interesting. A concern might arise that our tungsten carbide may have contained oxygen. Since our sample was not exposed to air after preparation, any residual oxygen should come from incomplete reduction of the starting material WO_3. Besides, the WC sample of Miyazaki et al. was confirmed to be free of oxygen by X-ray photoelectron spectroscopy [9]. Thus the formation of $HCOOCH_3$ seems to be characteristic of tungsten carbides, as it is of copper.

Temperature-Programmed Reactions

Temperature-programmed reactions (TPR) on porous material in the presence of a carrier gas could be quite different from those with single crystals under UHV conditions because of gas readsorption and diffusional mass transfer [25]. In the present study, therefore, no attempt was made to obtain kinetic information from TPR. We are only interested in the selectivity pattern of the reaction. In this regard, the TPR of CH_3OH on our tungsten carbide sample is consistent with the TPR of CH_3OH on W(100) with a C overlayer [10] in that CO was obtained in both cases as a major product in a similar temperature region. What then is the origin of the great difference in selectivity for the reaction of CH_3OH in a catalytic mode and in TPR?

It has been proposed that in methanol reactions on solid surfaces with an adsorption site denoted by $*$, $HCOOCH_3$ is formed either by dimerization of adsorbed formaldehyde intermediates CH_2O* [3], or by the reaction between an adsorbed methoxy intermediate CH_3O* and CH_2O* [5,10]. In either case, two surface intermediates must be adjacent to form $HCOOCH_3$. This condition is easily satisfied in catalytic reactions where gas phase methanol replenishes the surface with those intermediates to keep high surface coverage. In TPR where low surface coverage prevails through most of the run, there is a higher probability that an isolated intermediate would decompose to CO and H_2, rather than combine with another to form $HCOOCH_3$. Indeed, Ko et al. [10] noted that the small amount of $HCOOCH_3$ they observed in TPR on W(100)–(5 × 1)C was formed only when the surface concentration of the reactants was high.

The TPR method has been widely used to understand the nature of the surface reactions. But when comparing TPR of a molecule to the corresponding catalytic reaction of that molecule, however, the influence of surface coverage on both rate and selectivity must be kept in mind. This effect is well illustrated by the decomposition of formic acid over copper, nickel, and copper-nickel alloys [26], both in a catalytic mode and in TPR.

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