Methane Conversion to Methanol Using Au/ZSM-5 is Promoted by Carbon

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ABSTRACT: The oxidation of methane using molecular oxygen as the terminal oxidant, over a Au/ZSM-5 catalyst, has been previously shown to produce methanol and acetic acid as products. We now show that this reaction is significantly enhanced by the addition of a range of carbon additives. Isotopic ^{13}C-labeled studies and corresponding investigation into the activity of the carbon materials alone reveal that nearly all the methanol produced is derived from methane oxidation, with a negligible contribution attributed to the carbon additives, while further study identified carbon as the primary source of acetic acid, which was observed as a minor product. Gas phase CO is not observed as a product in the reaction of Au/ZSM-5 with $CH_4 + O_2$, and in reactions with added CO, not all the CO is converted. We, therefore, conclude that the effect observed with the carbon additive is not due to the in situ production of gas phase CO as a reaction intermediate. Rather, we postulate that the effect derives from the oxidation of the surface of the carbon in the aqueous reaction mixture and the interaction of the oxidized carbon surface with Au/ZSM-5. The reactivity of carbon in this reaction at 240 °C is unexpected, and the presence of water is required to observe the effect.

KEYWORDS: methane oxidation, low temperature, liquid phase, Au nanoparticles, carbon
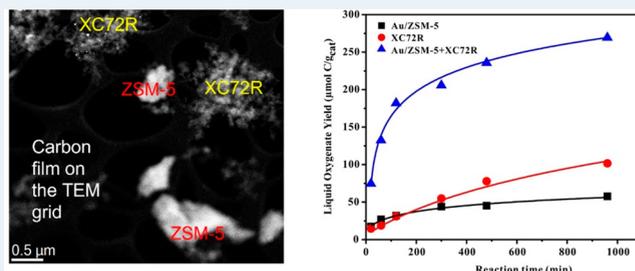
INTRODUCTION

The selective oxidation of methane to methanol or other valuable oxygenated products represents, for many, a grand challenge in catalysis. Indeed, it has often been considered a dream reaction for industrial catalysis, and more recently it can be considered to be of potential benefit to valorize emissions of natural gas that are currently flared.[1] In recent years, a major focus for the selective oxidation of methane has been placed on the use of lower reaction temperatures (<300 °C) in order to suppress nonselective oxidation pathways. A notable step forward in selective methane oxidation was demonstrated by Periana and co-workers, who showed that electrophilic Hg and Pt-complexes could oxidize methane in oleum,[2,3] forming methyl hydrogen sulfate which could subsequently be separately hydrolyzed to generate methanol and sulfuric acid. While these schemes would require multiple process steps, this pioneering work showed that by careful reaction and catalyst design, the reaction could be achieved.

Recently interest has shifted to using metal-exchanged zeolitic materials as catalysts. Notable examples include Fe-ZSM-5[4−7] and FeCu-ZSM-5[8,9] which are able to offer high selectivity toward CH_3OH when using either N_2O or H_2O_2 as oxidant. Alternatively, Cu-mordenite[10] and Rh-ZSM-5[11,12] are both able to produce CH_3OH with O_2 when using CO as a co-reductant. AuPd alloys, either immobilized onto a support such as ZSM-5[13] or unsupported, also demonstrate activity when using H_2O_2.[14] However, notably for all these examples, no selective oxygenate products are formed with O_2 alone, and hence either a more active oxidant (H_2O_2, N_2O) or a reducing agent (H_2, CO) is required.

Cu-mordenite catalysts can be operated in a two-stage catalytic cycle to form CH_3OH.[15−17] In this case, an oxidized Cu species is reacted with CH_4 forming a surface methoxyl which is subsequently extracted at a lower temperature with water. Subsequently, van Bokhoven and co-workers demonstrated[18] that Cu-mordenite can oxidize CH_4 with a continuous flow of H_2O to produce methanol; however, this reaction was stoichiometric. Roman-Leshkov and co-workers[19,20] have shown that Cu-mordenite can oxidize methane in a continuous flow of H_2O and O_2 with a closed catalytic cycle. In addition, Koishybay and Shantz[21] have demonstrated that

when using Cu-SSZ-13 as a catalyst, it is H_2O that is the source of the oxygen in the synthesized methanol.

Gold catalysts have been found to have exceptional activity in selective oxidation,[22] and most recently we have reported[23] that the oxidation of CH_4 using O_2 can be achieved in the absence of a co-reductant (H_2 or CO) in a closed catalytic cycle when using Au supported on ZSM-5 with high selectivity to oxygenated products achieved at reaction temperatures between 120 and 240 °C. In this initial study, we showed the active site for the reaction was gold nanoparticles (≥ 6 nm in diameter) supported on the exterior surface of the zeolite. Most interestingly, acetic acid was observed as the main selective oxidation product, which is in contrast to all previous studies where methanol is the main product. Using detailed isotopic studies (D and ^{13}C), we confirmed that the mechanism by which acetic acid was formed involved a surface coupling reaction between two C_1 species. The formation of acetic acid was enhanced by the addition of CO, and in this case, the methyl carbon of the acetic acid was derived from methane and the carboxyl carbon was mostly derived from the cofed CO. With these earlier studies in mind,[23] in particular those which utilize CO as a co-reductant, we now investigate the effect of the addition of a range of carbon sources on the oxidation of methane with O_2 using Au/ZSM-5 as a catalyst and demonstrate that the addition of carbon has a marked and unexpected effect on the observed catalysis.

■ EXPERIMENTAL METHODS

Note on Safe Operation of Experiments. When conducting catalytic oxidation, it is important to ensure that reaction conditions are such that the experiments are not conducted in the explosion region. For methane oxidation, Cooper and Wiezevich[24] have shown that experiments conducted with $\leq 14\%$ O_2 even at elevated temperature and pressure are outside the explosive region, and this is the case in the work reported here.

Catalyst Preparation. *Materials.* NH$_4$-ZSM-5 zeolite (SiO$_2$/Al$_2$O$_3$ = 25) was obtained from Nankai University Catalyst Co., Ltd. Gold(III) chloride trihydrate (HAuCl$_4$·3H$_2$O, $\geq 49.0\%$ Au basis) was purchased from Merck. Aqueous ammonia (25−28%), sodium carbonate (99.8%), sodium hydroxide ($\geq 96\%$) and hydrochloric acid (37%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Methane (99.999%) was obtained from Dalian Special Gases Co., Ltd. Nitrogen (99.999%) and oxygen (99.999%) were obtained from Wuhan Huaxing Industrial Gas Co., Ltd. ^{13}CH$_4$ (^{13}C, 99%, 99.9% chemical purity) was purchased from Cambridge Isotope Laboratories, Inc. Poly(vinyl alcohol) (PVA) (MW ≈10,000, 80% hydrolyzed) was obtained from Aldrich.

Several carbons were used in this experimental program, including XC72R (Cabot) and Black Pearls (Cabot), in addition to a series of functionalized graphitic carbons (Haydale) and oxidized Norit ROX 0.8-based carbons. The naming convention used for the functionalized graphitic carbons is based on the oxygen/carbon ratio as determined by XPS. For the Norit ROX 0.8-based carbons, the nomenclature refers to the carbon:potassium permanganate ratio utilized in the oxidation of these materials, so for the sample termed Norit ROX 1:0.5, the carbon (5g) was modified by the presence of potassium permanganate (2.5 g).

With the exception of the Norit ROX 0.8-based carbons, all materials and reagents were used directly without purification.

The procedure to modify the Norit ROX 0.8 carbons is outlined below.

Preparation of Oxidized Carbons. Ground activated carbon (AC) was oxidized according to a previously reported modified Hummers method.[25,26] AC (5 g) was added to a mixture of concentrated sulfuric (88 mL) and nitric acid (28 mL) under vigorous stirring and allowed to cool to 10 °C in an ice bath. Nitric acid was used in place of sodium nitrate to eliminate sodium contamination from the final material. Potassium permanganate (2.5 or 7.5 g) was added stepwise over a period of 2 h with the temperature maintained below 10 °C. The mixture was then allowed to reach room temperature over a period of 4 h, followed by heating to 35 °C for 30 min. Deionized water (250 mL) was added, causing the temperature to rise to 70 °C. After 15 min, a further portion of deionized water (1 L) was added, followed by the addition of 3% hydrogen peroxide to quench the residual oxidant. The mixture was allowed to settle overnight after which the sample was separated and washed repeatedly via centrifugation until a neutral pH was obtained. The sample was finally dried at 30 °C under vacuum for 16 h. An analogous water-washed sample was also prepared; AC (5.0 g) was added to 1L of water and stirred vigorously for 6 h. The sample was then separated via centrifugation and dried at 30 °C under vacuum for 16 h.

Catalyst Synthesis. Prior to Au deposition, the as-received zeolitic material (NH$_4$-ZSM-5) was first exposed to an oxidative heat treatment (450 °C at 3 °C/min for 6 h).

0.5 wt % Au loaded catalysts were prepared by a deposition-precipitation method using aqueous ammonia as the base to control the pH value.[23] This method was used to ensure the catalysts prepared contained no adventitious carbon impurities. Typically, ZSM-5 (3.0 g) was dispersed in deionized water (200 mL) and was mixed with a known amount of HAuCl$_4$ (6.0 mmol/L, aqueous solution) with stirring at 600 rpm. An appropriate amount of 2.5 wt % aqueous ammonia solution was slowly added until pH 6 was achieved. This step took more than 30 min at room temperature. The resulting solution was aged (60 °C, 2 h) with stirring (600 rpm), and the final pH value was around 5. The solid was collected by filtration, washed with deionized water, dried in air (60 °C, 16 h) and calcined (static air, 90 min, 240 °C, 3 °C/min). All the Au-ZSM-5 samples had 0.5 wt % Au loading unless otherwise stated.

An additional catalyst was prepared in an analogous manner in the presence of PVA. An aqueous solution of PVA (PVA (1.0 g) in water (50 mL)) was mixed with ZSM-5 (3.0 g) dispersed in deionized water (150 mL). The subsequent procedure was identical to that described above for the Au/ZSM-5 catalyst, with the resulting catalyst denoted PVA-Au-ZSM-5.

Catalyst Characterization. XPS was performed on a Thermo Fisher Scientific K-alpha$^+$ photoelectron spectrometer. Samples were mounted in small recesses within the Thermo Scientific copper powder plate. Samples were analyzed using a microfocused monochromatic aluminum X-ray source operating at 72 W (6 mA × 12 kV) using the 400 μm spot option, which is an elliptical area of approximately 400 μm × 600 μm. Data were recorded at pass energies of 200 eV for survey scans and 50 eV for high-resolution scans with 1 and 0.1 eV step sizes, respectively. Where required, charge compensation of the sample was achieved using a combination of both low-energy electrons and argon ions, which results in a C(1s) energy for the carbon support of 284.5 eV, typical of graphitic-like

Table 1. Comparison of Methane Oxidation Using Au/ZSM-5 and PVA-Au/ZSM-5 Catalysts[a]

| Catalyst | Reactants CH$_4$, O$_2$, CO (bar) | Productivity (μmol/g$_{cat}$) | | | | | Oxygenate selectivity (%) | Methanol Sselectivity in liquid (%) | Oxygenate productivity (μmol/g$_{cat}$) |
		Methanol	Methyl hydroperoxide	Acetic acid	Peracetic acid	CO$_2$			
Au/ZSM-5	20.7, 3.5, 0	9.72	0.6	7.5	3.3	20.0	61.4	30.5	21.1
PVA-Au/ZSM-5	20.7, 3.5, 0	21.3	2.0	50.7	5.5	93.6	59.2	15.7	79.5

[a]Reaction conditions: Catalyst (0.1 g,), H$_2$O (15 mL), 240 °C, 2 h, CH$_4$ (20.7 bar) and O$_2$ (3.5 bar), 1000 rpm.

Table 2. Influence of Carbon on Methane Oxidization over Au/ZSM-5 Catalyst[a]

| Entry | Carbon additive | Productivity (μmol/g$_{cat}$) | | | | | Oxygenate selectivity (%) | Methanol selectivity in liquid (%) | Oxygenate productivity (μmol/g$_{cat}$) |
		Methanol	Methyl hydroperoxide	Acetic acid	Peracetic acid	CO$_2$			
1	Au/ZSM-5	9.7	0.6	7.48	3.29	20.0	61.4	30.5	21.1
2	Au/ZSM-5+Norit Rox 0.8	111	0	14.9	0	2155	6.13	78.8	126
3	Norit Rox 0.8*	4.83	b.d.	9.81	b.d.	1805	1.34	19.76	14.6
4	Au/ZSM-5+Norit Rox washed	93.1	0	28.6	0	3555	4.06	61.9	122
5	Au/ZSM-5+Norit Rox 1:0.5	68.4	0	98.0	0	5108	4.92	25.9	166
6	Au/ZSM-5+Norit Rox 1:1.5	53.9	0	114	0	4830	5.50	19.2	167
7	Norit Rox 1:1.5*	9.38	b.d.	77.8	b.d.	3158	4.96	5.69	87.1
8	Au/ZSM-5+ Graphitic O/C = 0.067	82.4	4.61	83.4	3.29	2111	10.9	31.7	174
9	Au/ZSM-5+ Graphitic O/C = 0.186	120	5.66	144	7.95	2387	15.3	27.9	278
10	Au/ZSM-5+ Graphitic O/C = 0.170	177	4.52	183	9.04	3623	13.53	31.3	374
11	Graphitic O/C = 0.170*	5.87	2.15	121	2.79	2378	9.67	2.31	131
12	Au/ZSM-5+ Graphitic O/C = 0.183	148	3.78	162	4.64	3240	13.0	30.5	318
13	Au/ZSM-5+ Graphitic O/C = 0.185	117	3.50	114	4.23	2350	13.22	32.7	239
14	Au/ZSM-5+Black Pearls	159	b.d.	20.4	b.d.	2390	7.7	79.6	180
15	Au/ZSM-5+XC72R	156	b.d.	13.0	b.d.	784	18.8	85.7	169
16	XC72R*	9.58	b.d.	4.62	b.d.	501	3.62	50.9	14.2

[a]Reaction conditions: Au/ZSM-5 (0.1 g), carbon (0.08 g), H$_2$O (15 mL), 240 °C, 2 h, 1000 rpm. b.d.: below detection limit. * denotes the use of carbon (0.08 g) only, in the absence of the Au/ZSM-5 catalyst. These carbons were chosen as they represent a range of oxygen functionality.

carbons. Data analysis was performed in CasaXPS (v. 2.3.25)[27] using transmission corrected data converted from the Thermo Avantage software. Peak areas were corrected using Scofield cross sections[28] after removal of a Shirley-type background. Electron mean free paths are calculated using the TPP-2 M equation.[29]

N$_2$-physisorption analyses were performed on a Micromeritics 3Flex instrument at 77 K. Prior to analysis, ca. 0.15 g of the sample was degassed at 200 °C under a vacuum for 24 h. Free space was measured postanalysis using He. The Brunauer–Emmett–Teller model was used to determine the specific surface area under the relative pressure range of 0.05–0.30. Total pore volume (V_{pore}) was estimated from the adsorption branch of the isotherm at P/P_0 = 0.98. The microporous volume (V_{micro}) was estimated from the t-plot. Pore volume distribution was estimated using the BJH model.

Au content in the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Agilent 700 spectrometer.

STEM high-angle annular dark-field (HAADF) imaging was performed at the National University of Singapore, using an aberration-corrected JEOL ARM200CF microscope equipped with a cold field-emission gun operating at 200 kV.

The carbon content of PVA-Au-ZSM-5 was determined by using thermogravimetric analysis (TGA) on a Mettler DSC3+ instrument. The adsorbed water was removed by heating the sample in a nitrogen flow at temperature below 140 °C. In the temperature range from 140 to 800 °C, the gas flow was switched to zero-air for a complete degradation of the residual carbon. The carbon content was determined by measuring the weight loss under the zero-air condition.

Catalyst Testing. Methane oxidation with oxygen was carried out in a 25 mL stainless steel Parr autoclave reactor. In general, the catalyst (0.1 g), carbon (typically 0.1 g) and H$_2$O (15 mL) were transferred into the reactor, which was subsequently sealed and purged with N$_2$ for >30 min at 2 bar pressure to remove dissolved gases. After purging three times with methane, the reactor was pressurized with a gas mixture of methane and oxygen. The total pressure was set at

Table 3. Control Reactions for Methane Oxidation Using XC72R and Au/ZSM-5[a]

| Entry | Catalyst | Reactants CH_4, O_2, N_2 (bar) | Productivity ($\mu mol/g_{cat}$) | | | | | Oxygenate selectivity (C_{mol}%) | Methanol selectivity in liquid (%) | Oxygenate productivity ($\mu mol/g_{cat}$) |
			Methanol	Methyl hydro peroxide	Acetic acid	Peracetic acid	CO_2			
1	XC72R	0, 0, 24.2	0.1	b.d.	0.5	b.d.	8.5	11.5	9.1	0.6
2	XC72R	24.2, 0, 0	1.5	b.d.	0.9	b.d.	6.0	35.5	45.5	2.4
3	XC72R	0, 3.5, 20.7	b.d.	b.d.	b.d.	b.d.	716	–	–	0
4	Au/ZSM-5 + XC72R	0, 3.5, 20.7	b.d.	b.d.	12.5	b.d.	830	2.92	–	12.5
5	XC72R	20.7, 3.5, 0	9.58	b.d.	4.62	b.d.	501	3.62	50.9	14.2

[a]Reaction conditions: Entries 1−3: XC72R (0.1 g); entry 4: Au/ZSM-5 (0.1 g), XC72R (0.08 g); and entry 5: XC72 (0.08 g) H_2O (15 mL), 240 °C, 2 h, 1000 rpm. b.d.: below detection limit.

Table 4. CH_4 Oxidation in the Presence of XC72R and Au/ZSM-5[a]

| Entry | Catalyst | Productivity ($\mu mol/g_{cat}$) | | | | | XC72R conversion (%) | Oxygenate selectivity (%) | Methanol selectivity in liquid (%) | Oxygenate productivity ($\mu mol/g_{cat}$) |
		Methanol	Methyl hydroperoxide	Acetic acid	Peracetic acid	CO_2				
1	Au/ZSM-5	9.72	0.6	7.5	3.3	20.0	0	61.4	30.4	21.1
2	Au/ZSM-5+ XC72R (0.005 g)	28.1	1.4	9.8	0	70.7	0.7	61.4	30.4	21.1
3	Au/ZSM-5+ XC72R (0.02 g)	43.4	0	7.3	0	142	0.3	41.0	57.2	39.2
4	Au/ZSM-5+ XC72R (0.06 g)	95.8	b.d.	12.1	b.d.	357	0.3	28.9	74.8	50.7
5	Au/ZSM-5+ XC72R (0.08 g)	156	b.d.	13.0	b.d.	784	0.5	25.2	79.8	107
6	Au/ZSM-5+ XC72R (0.1 g)	167	b.d.	16.0	b.d.	895	0.4	18.8	85.7	169
7	Au/XC72R (0.08 g)	81.7	b.d.	7.7	b.d.	651	0.3	18.2	83.9	183

[a]Reaction conditions: Catalyst (0.1 g), XC72R (0−0.1 g), H_2O (15 mL), 240 °C, 2 h, CH_4 (20.7 bar) and O_2 (3.5 bar), 1000 rpm. b.d. below detection limit.

24.2 bar with varied methane and oxygen partial pressures measured at room temperature. The mixture was initially stirred at 1000 rpm for 10 min at room temperature and the pressure remained constant at around 24 bar. The reactor was then heated to the required reaction temperature and stirred at 1000 rpm for a predermined period, typically 2 h. After this time, the stirring was stopped, and the reactor cooled in ice water to a temperature below 10 °C in order to minimize the loss of volatile products. Gaseous reagents in the head space of the reactor were collected for analysis in a gas sampling bag at the end of a reaction. Liquid products were sampled using a glass syringe with Teflon filter head and analyzed via NMR. For reactions involving the addition of carbon, the specified carbon was added together with the catalyst at the start of the reaction.

In all cases, reactions were run multiple times over multiple batches of catalyst, with the data presented as an average of these experiments. Catalytic activity was determined to be consistent within ±5% on the basis of multiple reactions.

Isotopic Tracer Experiments. To trace the fate of carbon atoms from methane and to distinguish their fate from that of the added carbon, ^{13}C-labeled CH_4 was used in the reaction with oxygen. A high-sensitivity NMR CryoProbe on a Bruker Avance-600 liquid NMR spectrometer was employed to analyze the liquid products obtained from the isotopic tracing experiments. ^{1}H NMR spectra were recorded using a water suppression pulse sequence. The gas composition after the reaction was analyzed by a Hiden HPR-20 mass spectrometer.

■ RESULTS AND DISCUSSION

Initially we investigated the performance of a Au/ZSM-5 catalyst toward the oxidation of methane using a catalyst prepared via deposition precipitation (Table 1). As we have reported previously,[23] methane is oxidized to both C_1 and C_2 products. The Au/ZSM-5 catalyst was prepared using deposition precipitation in the absence of any sources of adventitious carbon, since the presence of such carbon could mask the effects we sought to observe for methane oxidation. Next, we prepared a similar Au/ZSM-5 catalysts using a sol-immobilization procedure, in order to determine the effect of a catalyst prepared with the addition of a source of carbon in the form of PVA (PVA-Au/ZSM-5). TGA analysis revealed that this catalyst contained approximately 64 mg/g of adventitiously added carbon (Figure S1). Subsequent determination of the performance of the PVA-Au/ZSM-5 catalyst toward methane oxidation (Table 1) revealed that the presence of the added carbon in the PVA-Au/ZSM-5 catalyst led to a significant enhancement in the yield of the oxygenated products as well as CO_2. As PVA is an oxygenate, the enhanced formation of such products is not a surprising observation and is in keeping with our prior studies into Fe-based catalysts comprising organic ligands for methane oxidation, where the presence of the ligand led to a false impression of any underlying methane conversion.[30] However, this interesting observation led us to investigate the addition of carbon in a controlled way to this catalyzed reaction.
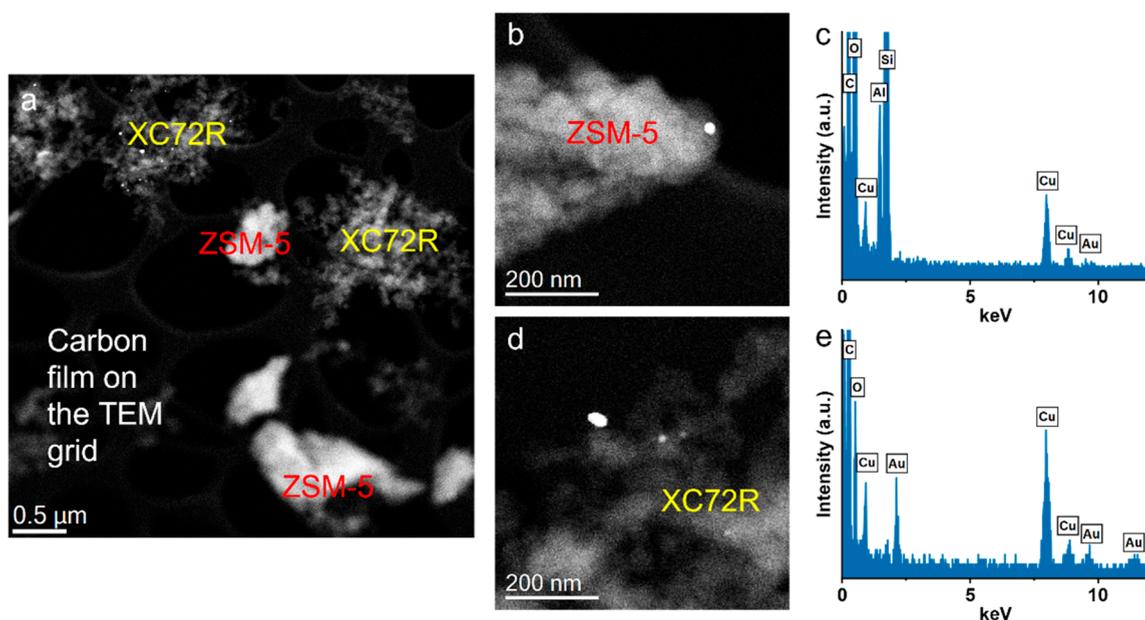
Figure 1. AC-STEM characterization of the Au/ZSM-5 and XC72R (0.08 g) catalyst after the methane oxidation reaction. (a) A lower magnification HAADF-STEM image, showing XC72R particles and ZSM-5 particles in the same field of view. (b, c) HAADF images and the corresponding X-ray energy dispersive spectrum of (b, c) a ZSM-5 particle and (d, e) a XC72R particle.

We subsequently conducted a series of methane oxidation studies utilizing a physical mixture of the Au/ZSM-5 catalyst and a range of carbon additives (Table 2, with textural properties of the carbons reported in Table S1). In a manner similar to that seen over the PVA-Au/ZSM-5 catalyst, a significant increase in both oxygenate productivity and CO_2 yield was observed, regardless of the carbon utilized. Notably, control experiments demonstrated that the increased production of methanol over the physical mixture systems was not a result of the separate activity of the individual components, i.e., the sum of the activities of separate experiments with Au/ZSM-5 and the carbon (with CH_4 + O_2) was considerably lower than when the Au/ZSM-5 and carbon were utilized together as a physical mixture. However, it is interesting to note that a significant proportion of acetic acid production (a minimum of 65% in all cases studied) may be attributed to the carbon additives (Table 2). XPS analysis of the fresh carbons (Table S2, Figure S2 and accompanying supplementary text) allows for the classification of the carbon additives into three categories of low, intermediate and high oxygen functionality. However, there is no clear relationship between the observed activity toward methanol (or total oxygenate) production and the extent of carbon oxidation that could be used to correlate the activities observed.

We subsequently set out to gain a greater understanding of the observed improvement in reactivity, with a particular focus on the physical mixture of Au/ZSM-5 and XC72R carbon, a material we have extensively investigated as a support for precious metal nanoparticles.[31] Under an inert atmosphere or in the absence of O_2, negligible concentrations of oxygenates were detected over the XC72R carbon alone (Table 3, entries 1 and 2). However, upon the introduction of O_2, a significant amount of CO_2 was detected (Table 3, entry 3). By comparison, when the Au/ZSM-5 catalyst was utilized in the presence of O_2 and XC72R, but in the absence of methane (Table 3, entry 4), a relatively small amount of acetic acid was observed in addition to CO_2.

When CH_4 was reacted with O_2 in the presence of a physical mixture of Au/ZSM-5 and XC72R (Table 4, Figure S3), significant amounts of methanol were detected, over and above that observed over the Au/ZSM-5 catalyst alone (Table 4, entry 1). A strong correlation between the amount of XC72R utilized and oxygenate productivity was observed (Table 4, entries 2−6), although, notably, the effect on the yield of acetic acid was not very marked. In all cases and, perhaps unsurprisingly, given the contribution of the XC72R alone (Table 3), a pronounced enhancement in CO_2 production was also detected. Using XC72R as a support for the Au nanoparticles, with the catalyst prepared using an identical deposition procedure to that used for the Au/ZSM-5 analogue, led to an increase in the yield of methanol (Table 4, entry 7) compared to that observed over the Au/ZSM-5 catalyst alone. However, this was not as pronounced as that observed over a physical mixture of Au/ZSM-5 and XC72R, indicating that the zeolite plays an important role in the catalysis. Importantly, this experiment demonstrated that if any Au was transferred during the reaction from the ZSM-5 support to the carbon then it would not have a substantial effect on the observed reactivity. We investigated the possibility of such Au transfer using aberration-corrected microscopy. Selected catalysts were characterized using aberration-corrected scanning transmission electron microscopy (AC-STEM). Figure S4 shows the representative HAADF STEM images of the Au/ZSM-5 catalyst before and after use in the methane oxidation reaction. The Au nanoparticles can be clearly observed via the atomic number (Z) contrast. These STEM results suggest the catalysts mostly contain Au nanoparticles. Neither sub-nm nor atomically dispersed Au species were detected, which is consistent with our recent report.[23] The physical mixture of Au/ZSM-5 and XC72R (0.08 g) was also investigated after use in the methane oxidation reaction, via AC-STEM (Figure 1). Figure 1a shows a lower magnification HAADF-STEM image that has both ZSM-5 particles (brighter contrast) and XC72R particles (less bright contrast). Figure 1b−e shows HAADF-STEM

Table 5. Effect of Reaction Temperature on Methane Oxidation Using Au/ZSM-5 Catalyst in Addition to XC72R[a]

			Productivity (μmol/g_{cat})							
Entry	Catalyst	Temperature (°C)	Methanol	Methyl hydroperoxide	Acetic acid	Peracetic acid	CO_2	Oxygenate selectivity (%)	Methanol selectivity in liquid (%)	Oxygenate productivity (μmol/g_{cat})
1	Au/ZSM-5+ XC72R	120	2.3	2.6	1.0	b.d.	6.9	50.0	33.3	5.9
2	Au/ZSM-5	120	2.6	b.d.	2.8	1.2	2.8	79.1	24.5	6.6
3	Au/ZSM-5+ XC72R	160	8.5	b.d.	3.9	b.d.	44.8	26.7	52.2	12.4
4	Au/ZSM-5	160	2.1	0.7	4.6	1.5	4.3	77.7	4.7	8.9
5	Au/ZSM-5+ XC72R	240	156	b.d.	13.0	b.d.	784	18.8	85.7	169
6	Au/ZSM-5	240	9.72	0.6	7.5	3.3	20.0	61.4	30.4	21.1

[a]Reaction conditions: Au/ZSM-5 (0.1 g), XC72R (0.08 g), H_2O (15 mL), 2 h, CH_4 (20.7 bar) and O_2 (3.5 bar) 1000 rpm. b.d.: below detection limit.
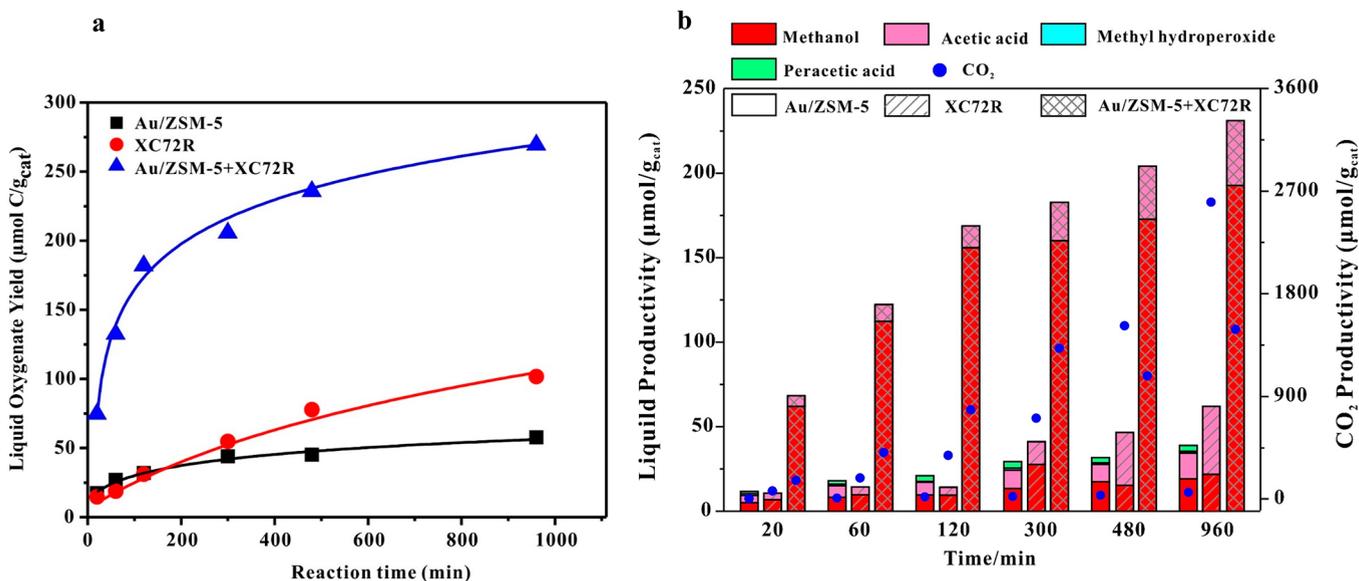
Figure 2. Promotional effect of XC72R addition on the catalytic performance of Au/ZSM-5, as a function of reaction time (a) total oxygenate yield, (b) liquid oxygenate and CO_2 productivity. Reaction conditions: Au/ZSM-5 (0.1 g), XC72R (0.08 g), H_2O (15 mL), 240 °C, CH_4 (20.7 bar), O_2 (3.5 bar), 1000 rpm.

Table 6. Influence of XC72R on the Analysis of Liquid Product in Methane Oxidation over Au/ZSM-5[a]

		Productivity (μmol/g_{cat})							
Entry	Catalyst	Methanol	Methyl hydroperoxide	Acetic acid	Peracetic acid	CO_2	Oxygenate selectivity (%)	Methanol selectivity in liquid (%)	Oxygenate productivity (μmol/g_{cat})
1	Au/ZSM-5	9.72	0.60	7.48	3.29	20.0	61.4	30.5	21.1
2	Au/ZSM-5+ XC72R (0.08 g)	9.71	0.56	7.48	b.d.	–	–	–	17.8

[a]Standard reaction conditions: Au/ZSM-5 (0.1 g), H_2O (15 mL), 240 °C, 2 h, 20.7 bar CH_4, 3.5 bar O_2, 1000 rpm. After a standard 2 h reaction over Au/ZSM-5 (entry 1), the reaction solution was split into two aliquots to one aliquot (entry 2), XC72R was added to the mixture and stirred for 10 min (1000 rpm at ambient conditions), then the liquid product was analyzed by ^{1}H NMR spectroscopy. b.d.: below detection limit.

images and the corresponding X-ray energy dispersive spectrum (X-EDS) of the two components. The presence of Au can be identified as bright particles on both the ZSM-5 and XC72R component in the HAADF-STEM images, with X-EDS analysis confirming the identity of the two support materials. The ZSM-5 support particle gave strong Al and Si X-ray signals (Figure 1c), which were absent from the XC72R particle (Figure 1e). These results strongly indicate that some of the Au species have migrated from the ZSM-5 support to the XC72R additive during the methane oxidation reaction and excludes any suggestion that the apparent migration of Au is an

artefact of the mode of analysis. However, it is important to note that the migration of Au from ZSM-5 to the XC72R is expected to lead to lower catalytic activity as explained earlier (Table 4, entry 7).

Further study demonstrated that the promotive effect of the carbon could be observed over a temperature range of at least 160−240 °C (Table 5). Comparisons of catalytic performance in the presence and absence of the XC72R additive over extended reaction times further highlights the relatively minor contribution from the carbon alone to liquid products (Figure 2a,b, Table S3). However, given the observed transfer of Au

Table 7. Influence of Reaction pH on the Methane Oxidization over a Physical Mixture of Au/ZSM-5 and XC72R[a]

			Productivity (μmol/g_{cat})							
Entry	Catalyst	pH	Methanol	Methyl hydroperoxide	Acetic acid	Peracetic acid	CO_2	Oxygenate selectivity (%)	Methanol selectivity in liquid (%)	Oxygenate productivity (μmol/g_{cat})
1		4 (HCl)	13.2	0.9	7.3	1.8	8.8	78.7	40.9	23.2
2	Au/ZSM-5	7	9.72	0.6	7.5	3.3	20.0	61.4	30.4	21.1
3		10 ($NH_3\cdot H_2O$)	3.2	1.1	6.1	2.4	3.8	85.0	15.0	12.7
4		4 (HCl)	129	b.d.	9.4	b.d.	386	27.7	87.3	138
5	Au/ZSM-5 + XC72R	7	156	b.d.	13.0	b.d.	784	18.8	85.7	169
6		10 ($NH_3\cdot H_2O$)	111	b.d.	14.7	b.d.	441	24.1	79.1	126

[a]Reaction conditions: Au/ZSM-5 (0.1 g), XC72R (0.08 g), H_2O (15 mL), 240 °C, 2 h, CH_4 (20.7 bar), O_2 (3.5 bar), 1000 rpm. The pH valve was adjusted by HCl or $NH_3\cdot H_2O$. The pH of the solution in the autoclave was measured before reaction. b.d.: below detection limit.

Table 8. Effect of Sequential Gas Recharging on Methane Oxidation Activity[a]

			Productivity (μmol/g_{cat})							
Entry	1st h	2nd h	Methanol	Methyl hydro peroxide	Acetic acid	Peracetic acid	CO_2[b]	Oxygenate selectivity (%)	Methanol selectivity in liquid (%)	Oxygenate productivity (μmol/g_{cat})
1	Au/ZSM-5	Au/ZSM-5	10.8	3.0	7.6	3.6	10.0 + 7.7 = 17.7	82.4	29.8	25.0
2	Au/ZSM-5	Au/ZSM-5 + XC72R	118	b.d.	12.7	b.d.	10.0 + 383 = 393	27.7	82.3	130
3	Au/ZSM-5	XC72R	11.4	b.d.	7.3	b.d.	10.0 + 227 = 237	9.9	43.9	18.7

[a]Reaction conditions: Au/ZSM-5 (0.1 g), XC72R (0.08 g), H_2O (15 mL), 240 °C, CH_4 (20.7 bar), O_2 (3.5 bar), 1000 rpm. All the reactions were reacted for 2 h. Au/ZSM-5 alone was used for the first hour, then the reaction was quenched by ice water to below 10 °C and gas products was collected. Entry 1: After an initial 1 h, reaction gaseous reagents were replaced and the reaction allowed to proceed for a further 1 h. Entry 2: After an initial 1 h reaction, XC72R (0.08 g) was introduced into the reactor, and gaseous reagents replaced. The reaction was allowed to proceed for a further 1 h. Entry 3: After an initial 1 h, reaction the Au/ZSM-5 catalyst was removed by centrifugation from the mixture. XC72R (0.08 g) was combined with the postreaction solution and reintroduced into the reactor, after the replacement of gaseous reagents the reaction was allowed to proceed for a further 1 h. b.d.: below detection limit. [b]CO_2: Sum of the CO_2 generated from the first hour (10 μmol/g_{cat}) and the second hour reactions.

between the ZSM-5 support and carbon additive (Figure 1), further study is still required in order to determine the effective lifetime of this system. Regardless the observed promotive effect achieved through carbon addition is noteworthy. As with our standard reaction (2 h), product yields obtained in the presence of a physical mixture of Au/ZSM-5 and XC72R were found to greatly exceed those observed when using either component alone. With the potential for XC72R to adsorb some of the products and therefore possibly mask the true extent of the observed effects a further experiment with the Au/ZSM-5 catalyst alone was conducted, as follows (Table 6). After the reaction, the postreaction mixture was cooled to room temperature and divided into two aliquots. The first was analyzed by ^{1}H NMR spectroscopy (Table 6, entry 1). To the second aliquot, XC72R (0.08 g) was added and the mixture stirred at ambient temperature for 10 min. Analysis of the second aliquot (Table 6, entry 2) demonstrated that XC72R did not affect the apparent product distribution, and hence product adsorption by the carbon can be discounted.

The effect of the reaction solution pH was subsequently investigated (Table 7) with the pH being adjusted between pH 4 and pH 10. A positive effect of adding XC72R was observed across the range of pH values investigated. In the case of the Au/ZSM-5 only experiments, an increase in reaction solution pH resulted in a decrease in the yield of oxygenated products, attributed to the partial dissolution of the ZSM-5 zeolite under more basic conditions, whereas when XC72R was present a maximum product yield was observed at pH 7.

A further set of experiments were conducted in which the Au/ZSM-5 catalyst was used to react CH_4 with O_2 under standard reaction conditions at 240 °C. After 1 h, the reaction was quenched using ice water to decrease the temperature below 10 °C and the gas products were collected. The gaseous reagents were replaced, and the reaction mixture was then subsequently reacted for a further 1 h (at 240 °C), in the presence of the Au/ZSM-5 catalyst and finally quenched and the products analyzed (Table 8, entry 1). In a separate reaction, XC72R was added to the second part of the reaction mixture (again with the retained Au/ZSM-5 catalyst) and similarly treated (Table 8, entry 2). In a third reaction mixture, the Au/ZSM-5 catalyst was removed by centrifugation, and XC72R was added and reacted for another 1 h (Table 8, entry 3). The production of CO_2 showed a marked increase when XC72R was added to the reaction mixture, in keeping with our earlier results (Table 2). However, only when both XC72R and Au/ZSM-5 were present did the methanol yield increase (Table 8, entry 2), while it was also demonstrated that that theXC72R carbon alone cannot facilitate the oxidation of methane under these reaction conditions (Table 8, entries 1 and 3). The addition of methanol at the start of the reaction in the presence of XC72R was found to have no effect, and hence under the reaction conditions, we have explored methanol is not reacted further by the carbon additive (Table S4).

Isotopically labeled $^{13}CH_4$ was used to determine the origin of the carbon in the methanol and CO_2 for the reaction when XC72R was added. The reaction data (Table S5) show that

within experimental error, identical liquid product profiles are observed for the reactions utilizing either $^{13}CH_4$ or CH_4. For the reaction with CH_4, the ^1H NMR signal of the methyl group
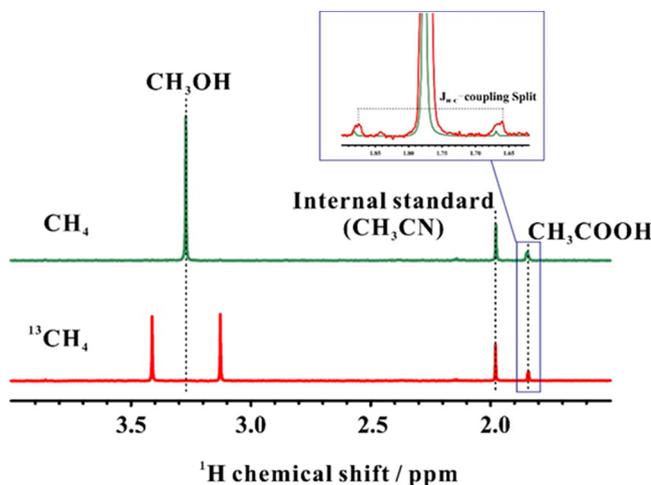

Figure 3. ^1H NMR spectra of the products obtained from the reactions using CH_4 in natural abundance or ^{13}C-labeled $^{13}CH_4$ as reactant. Insertion: Enlarged and normalized J_{H-C}-coupling region of the methyl group of acetic acid.

in methanol occurs at 3.27 ppm (Figure 3). In comparison, the ^1H NMR signal of methanol for the reaction with $^{13}CH_4$ is completely split into a doublet at 3.41 and 3.13 ppm owing to the *J*-coupling of the proton with the ^{13}C atom in the methyl group. This result supports our earlier investigations into the contribution of the carbon alone to the observed catalysis, with the negligible formation of methanol in the absence of the Au/ZSM-5 catalyst (Table 2, Table S2). Such studies indicate that the vast majority of the carbon in the methanol originates from CH_4. Likewise, based on these isotopically labeled experiments, we were also able to determine that the carbon additive is the primary source of acetic acid. Mass spectrometry analysis (Figure 4) shows that about 61.5% CO_2 originates from $^{13}CH_4$ and 38.5% from XC72R as determined by the comparison of the peak intensity of $^{13}CO_2$ and CO_2 obtained from the reaction using $^{13}CH_4$.

The experiment using ^{13}C-labeled methane helps to explain the origin of the marked enhancement in oxygenate production when carbon is used in conjunction with the Au/ZSM-5 catalysts. As the enhancement in methanol yield results almost entirely from the increased reaction of methane, it is apparent that the added carbon is not catalytically active and instead acts as a promoter for Au/ZSM-5.

We consider that, when used in conjunction with the Au/ZSM-5 catalyst, the carbon may act as a reducing agent and promote the formation of active oxo-species on the metal surface; however, the degree to which the Au/ZSM-5 catalyst and partially oxidized carbon additive must be in intimate contact for such a promotion to be achieved is still unclear.[22,30] Regardless, this observed enhancement is similar to the effect of adding CO as a reactant which has been well-reported to enhance the rate of oxidation of hydrocarbons over zeolite-supported metal catalysts.[11,23,32]

To determine the mechanism by which the carbon additive exerts its effect on the observed catalytic reaction, we subsequently carried out further experiments. First, as it is known that hydrogen peroxide can be an effective oxidant and it is possible that surface species on the carbon could be an effective source of hydrogen for hydrogen peroxide synthesis, we, therefore, analyzed the reaction mixture of Au/ZSM-5 with CH_4 + O_2 with XC72R and no hydrogen peroxide was observed. Next, we investigated whether it is the formation of gas phase CO, a well-reported promoter for supported metal-mediated methane activation,[11,23,32] as a reaction intermediate that is the origin of the effect. In the reaction of CH_4 + O_2 with Au/ZSM-5 in the presence of carbon, no gas phase CO is observed in the product stream (Figure S5). We then added CO to the reaction gases, and even when added in low amounts, the CO was not totally consumed (Table 9). Therefore, we conclude that the formation of CO released from the surface of the carbon as a reaction intermediate is not the source of the observed promotion. However, the promotive effect of adding carbon to the reaction mixture (Table 4) is similar to that of adding CO as both show a linear relationship between the enhancement in activity and the amount of carbon or CO added (Figure S6). An early study by Nelson Smith and co-workers[33] showed that the surface of carbon can be oxidized and functionalized by reaction with water at 200 °C, a temperature very similar to that used in our study. With this earlier work in mind and in an attempt to determine the
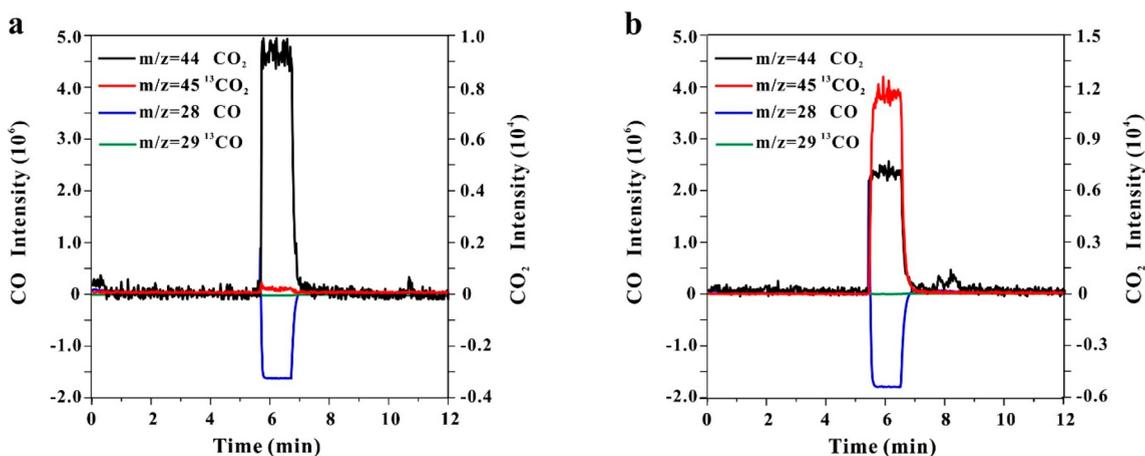

Figure 4. Mass spectrometry analysis of gas products obtained from the reactions using (a) $^{12}CH_4$ and (b) $^{13}CH_4$ as reactant.

**Table 9. CH$_4$ Oxidation on Au/ZSM-5 Catalysts[a]**

Entry	Reactants CH$_4$, CO, O$_2$ (bar)	Productivity (μmol/g$_{cat}$)					Added CO (μmol)	Residual CO (μmol)	CO conversion (%)[b]	Oxygenate selectivity (%)	Methanol selectivity in liquid (%)	Oxygenate productivity (μmol/g$_{cat}$)
		Methanol	Methyl hydroperoxide	Acetic acid	Peracetic acid	CO$_2$						
1	20.7, 0, 3.5	8.2	0.8	7.0	2.0	9.9	0.0	0.0	0.0	73.1	30.4	18.0
2	23.06, 0.14, 1	67.5	0.3	8.1	2.3	199.3	84.7	65.3	22.8	30.7	76.4	78.1
3	22.7, 0.5, 1	134.2	0.0	11.3	2.6	706.3	302.4	224.1	25.9	18.7	82.8	148.1
4	22.2, 1, 1	233.3	0.0	21.9	3.2	1289.6	604.8	505.2	16.5	18.0	82.4	258.3

[a]Reaction conditions: Catalyst (0.1 g), H$_2$O (15 mL), 240 °C, 1 h, 1000 rpm. [b]CO conversion (%) = (added CO − residual CO)/(added CO) × 100%.

chemical stability of the XC72R additive, we subsequently carried out detailed TPO studies of the XC72R carbon, with the as-received material observed to undergo oxidation at approximately 595 °C, with no significant variation observed for analogous samples after exposure to methane oxidation reaction conditions (Figure S7). However, additional XPS measurements of the fresh XC72R carbon and the same carbon after use in the methane oxidation reaction (in water at 240 °C) do indeed show that the surface of the carbon has been oxidized (Figure S8), with a clear increase in C−O/C−OH functionality observed after exposure to reaction conditions. We consider that it is the oxidized surface of the carbon that is the source of the enhancement in reaction that we observe (Scheme 1). In our recent paper[31] we reported that the

Scheme 1. Schematic Illustration on the Promotive Effect of Carbon Additives on the Methane Oxidation Catalyzed by Au/ZSM-5
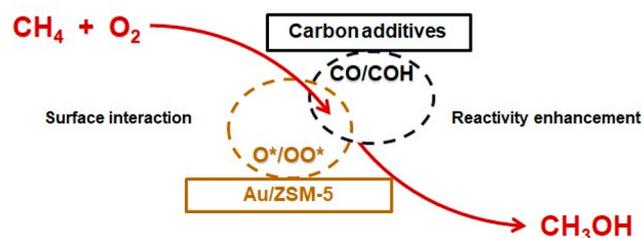
addition of XC72R to a physical mixture of Au/TiO$_2$ and Pd/TiO$_2$ in an aqueous reaction mixture enhanced the oxidation of an alcohol. This we considered to be due to a new cooperative enhancement effect which is ascribed to electron transfer between the Au and Pd aided by the conductivity of the XC72R. This shows that XC72R can readily interact with a supported Au catalyst when added as a physical mixture. Taking these observations as a whole, we now conclude that the effect we observe of the enhancement in methane oxidation with Au/ZSM-5 as a catalyst when XC72R is added is due to the surface of the XC72R being oxidized by water/O$_2$ at elevated reaction temperatures and it is this oxidized carbon surface interacting with the Au/ZSM-5 that facilitates the enhanced activity observed. Although we cannot rule out the involvement of a reducing species, for example, formaldehyde, transferring between the carbon and Au/ZSM-5, notably we do not observe any new liquid phase species in the presence of added carbon. We therefore postulate a direct interaction between the surfaces of the two materials and the surface species present upon them. These may include CO as an adsorbed species on the carbon, but it does not desorb. Hence,

we consider that the mechanism by which carbon acts in this reaction is not via the formation of gas phase CO in situ as a reaction intermediate, rather carbon and CO exert similar effects but do so via by different routes.

The reactivity of carbon in water at 240 °C in the oxidation of methane is an unexpected finding. Indeed, the oxidation of carbon when methane is present occurs at temperatures as low as 120 °C. It is possible that this observation may have some relevance to the design of catalysts with reduced coking during the oxidation of hydrocarbons.

■ CONCLUSION

The addition of a range of carbon additives to a Au/ZSM-5 catalyst has been shown to significantly enhance catalytic performance toward the oxidation of methane, when using O$_2$ as the terminal oxidant. The reaction produces both methanol and acetic acid as products together with CO$_2$. Notably, ^{13}C labelling studies show that while a considerable proportion of acetic acid production observed can be attributed to the carbon additive, the direct contribution of the carbon promoters to methanol formation is negligible. Indeed, our studies indicate that the carbon materials alone are not directly responsible for the observed improvement in oxygenate production and rather they act as a promoter for the Au/ZSM-5 catalyst. Notably, no direct correlation may be drawn between the extent of catalytic promotion and criteria such as surface area, purity or functionality of the as-received carbons. Rather, we attribute the observed enhancement in catalytic performance to the partial oxidation of the surface of the carbon, and it is the interaction of the oxidized carbon surface with the Au/ZSM-5 catalyst that is responsible for the observed improvement in catalytic performance. The presence of water is key in achieving the partial oxidation of the carbon additives at temperatures far lower than that which may be expected based on temperature programmed oxidation analysis of the pristine carbon materials.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.3c01226.

> Data relating to catalytic activity toward the selective oxidation of methane, with accompanying character-ization of catalytic materials and carbon promoters via TGA, XPS, HAADF-STEM, TPO as well as porosimetry analysis and surface area determination (PDF)

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Notes

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