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Chemical Titration and Transient Kinetic Studies of Site Requirements in Mo_2C-Catalyzed Vapor Phase Anisole Hydrodeoxygenation

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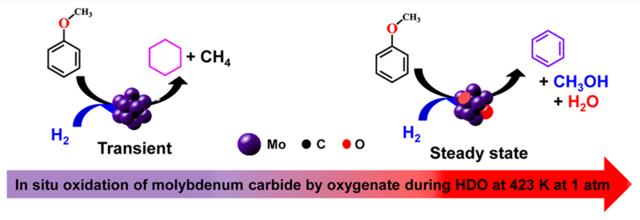
S *Supporting Information*



ABSTRACT: The turnover frequency (TOF) of benzene synthesis from vapor phase anisole hydrodeoxygenation (HDO), estimated via in situ CO titration, was found to be invariant ($1.1 \pm 0.3 \times 10^{-3}$ s^{-1}) over molybdenum carbide (Mo_2C) catalysts with varying CO chemisorption uptakes (~70 to ~260 μmol g^{-1}, measured ex situ at 323 K). Accumulation of oxygen (~0.29 monolayer) over Mo_2C catalysts was determined by an oxygen mass balance during the transient of anisole HDO at 423 K under ambient pressure (H_2/anisole molar ratio ~ 110). Similar product selectivity, apparent activation energy, and TOF of benzene synthesis for an oxygen treated (with oxygen incorporation: O/Mo_{bulk} (molar ratio) = 0.075) and freshly prepared Mo_2C catalysts (no exposure to air prior to kinetic measurements) demonstrate that the effect of oxygen at these low concentrations is solely to reduce the number of active sites for anisole HDO, resulting in a lower (~3 times) benzene synthesis rate per gram of catalyst for the oxygen-modified material. The observed benzene synthesis rates per CO chemisorption site for bulk molybdenum oxide (MoO_x) catalysts were found to be ~10 times lower than those for Mo_2C catalysts, suggesting that bulk molybdenum oxide phases are not associated with the dominant active sites for anisole HDO at 423 K under ambient pressure.

KEYWORDS: *molybdenum carbide, molybdenum oxide, hydrodeoxygenation (HDO), oxidation, anisole, benzene synthesis, in situ CO titration, oxygen treatment, turover frequency (TOF)*

1. INTRODUCTION

Lignin, a natural amorphous polymer consisting of phenolic compounds that comprise 15−30% by weight of biomass and 40% by energy, can be regarded as an alternative sustainable source for aromatic feedstock production, specifically, benzene, toluene, and xylene (BTX).[1,2] The conversion from phenolic compounds to aromatic hydrocarbons, however, requires the selective removal of oxygen heteroatoms and the concurrent preservation of aromaticity. Benzene, for example, can be produced from anisole, a model compound representing phenolic monomers derived from lignin, via selective cleavage of the phenolic C−O bond. Catalytic hydrodeoxygenation (HDO) can remove the oxygen as water; however, undesired C═C bond hydrogenation or C−C bond cleavage by hydrogenolysis can also concurrently occur. We have previously reported that molybdenum carbide (Mo_2C) catalysts can selectively convert anisole to benzene in the vapor phase at low reaction temperatures (423−520 K) with high benzene selectivity >90% (C_6^+ basis), no C_2−C_5 products, and very low cyclohexane selectivity (<9%, C_6^+ basis).[3]

Metallic sites on Mo_2C catalysts were identified to be involved in vapor phase anisole HDO based on the observed near invariance in benzene synthesis rates normalized by CO chemisorption sites measured ex situ at 323 K (average value: $3.4 \pm 1.0 \times 10^{-4}$ mol s^{-1} $mol_{COsite}{}^{-1}$),[3] suggesting that CO adsorption sites are associated with sites responsible for the activation of anisole. In this work, we use in situ CO titration to assess the turnover frequency (TOF) of benzene synthesis rates over Mo_2C catalysts with different CO chemisorption uptakes measured ex situ at 323 K (~70 to ~260 μmol g^{-1}) and report an average TOF of $1.1 \pm 0.3 \times 10^{-3}$ mol s^{-1} $mol_{COsite}{}^{-1}$, implying that only a fraction of the metallic sites probed by ex situ CO chemisorption studies is active for HDO catalysis on Mo_2C surfaces.

The oxophilicity of molybdenum carbide is evidenced from its pyrophoric nature[4−7] and the experimental observation of a $Mo_2C_{1.04}O_{0.88}$ composition, even after treating an air-exposed molybdenum carbide catalyst in a 3/1 (vol %) CH_4/H_2 mixture at 623 K for 1 h by Bell and co-workers.[6] DFT calculations by Rodriguez and co-workers also suggest that O_2 can bond strongly to both C and Mo sites of molybdenum carbides with corresponding adsorption energies of ~520 and ~786 kJ mol^{-1}.[8] The possibility of in situ oxidation of Mo_2C catalysts by oxygen-containing reactants during HDO, therefore, cannot be excluded. Transient kinetic measurements combined with temperature-programmed surface reaction with H_2 (TPSR)

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experiments of a spent Mo_2C catalyst after vapor phase anisole HDO were employed in this work to show that oxygen accumulation on/in Mo_2C catalysts occurs during HDO, even at a high H_2-to-anisole molar ratio (∼110) in the reactant feed at 423 K under ambient pressure.

Boudart and co-workers[9−11] reported that chemisorbed oxygen on/in tungsten carbide catalysts can introduce acidic sites, which increases the rate of alkane isomerization but inhibits the rate of alkane hydrogenolysis reactions, resulting in high alkane isomerization selectivity (70−99%). An oxycarbide phase of molybdenum was proposed to be responsible for high selectivity (∼85%) of *n*-heptane isomerization by Ledoux and co-workers.[12] Residual oxygen retained in molybdenum carbide catalysts, achieved by using different carburization temperatures for MoO_3 catalysts, was also found to suppress benzene hydrogenation rates.[3,13,14] Rodriguez and co-workers[8] have employed density functional theory (DFT) calculations to suggest that a Mo oxycarbide can be formed during the water gas shift reaction on the surface of Mo_2C in which chemisorbed oxygen, produced from water dissociation, is involved. These reports demonstrate that the presence of heteroatoms on/in transition metal carbide catalysts can alter their reactive functionality by introducing acidic sites or by changing the number of active centers available for catalysis.

In this study, we investigate the effect of oxygen incorporation on/in molybdenum carbide catalysts on the kinetics of vapor phase anisole HDO. An oxygen-treated molybdenum carbide catalyst with oxygen uptake O/Mo_{bulk} (molar ratio) = 0.075 showed an ∼3 times lower benzene synthesis rate per gram of catalyst (2.4×10^{-8} vs 6.8×10^{-8} mol s^{-1} g^{-1}) as compared with a freshly prepared molybdenum carbide catalyst in which the catalyst was not exposed to oxygen before reaction. A similar TOF of benzene synthesis, obtained by in situ CO titration, was found for both the oxygen-treated and freshly prepared molybdenum carbide formulations, suggesting that the effect of oxygen is to solely reduce the number of active sites for vapor phase anisole HDO.

2. EXPERIMENTAL METHODS

2.1. Catalyst Synthesis. Mo_2C catalysts were prepared by a temperature-programmed reduction method similar to those reported previously.[3,7,15] Briefly, ∼1.6 g of ammonium molybdate tetrahydrate (AMT, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ sieved, 177−400 μm, Sigma, 99.98%) was loaded into a tubular quartz reactor with a thermocouple attached to a thermowell (i.d. 10 mm) and purged with a flow of a CH_4 (Matheson, 99.97%)/H_2 (Minneapolis Oxygen, 99.999%) gas mixture (15/85, vol %, total flow rate ∼2.75 cm^3 s^{-1}) for 1−5 min at room temperature (hereafter denoted as RT) and then heated in a three-zone split tube furnace (series 3210, Applied Test System) with a typical temperature protocol (15% CH_4/H_2, RT (1.5 h) to 623 K [5 h] (1.5 h) to 873 K [3 h], cool) that is described in detail below. The reactor was heated from RT to the first target temperature (∼623 K) within 1.5 h, and the temperature was then held for 5 h. Subsequently, the sample was heated to the second target temperature (∼873 K) within 1.5 h and held at this temperature for 3 h prior to being cooled to RT in the same CH_4/H_2 gas mixture flow. The resulting material (Mo_2C) was then treated in a flow of 1% O_2/He mixture (Matheson, Certified Standard Purity) at ∼1.67−3.33 cm^3 s^{-1} to passivate the carbidic surface.[4,7,15] The reactor temperature was found to increase from RT to ∼333−373 K upon the introduction of a 1% O_2/He gas mixture, confirming the pyrophoric feature of as-synthesized Mo_2C catalysts.[4,7,16] After the sample was cooled to RT (typically 20−30 min), the passivated Mo_2C catalyst was removed from the reactor. Multiple batches of Mo_2C synthesized using the same preparation conditions were mixed in order to (i) create a representative Mo_2C catalyst that shares a set of physical/chemical properties and (ii) perform in situ CO titration experiments (section 2.4) and transient kinetic measurements (section 2.5), which required large amounts of sample (0.43 to 8.5 g) for quantitative analysis using online mass spectrometry (MKS Cirrus 200 Quadrupole MS system).

A Mo_2C catalyst, which was not exposed to air (i.e., the passivation step was omitted), was also prepared according to the temperature protocol described above, except that the sample was cooled in a flow of H_2 (total flow rate of 2.3 cm^3 s^{-1}) from 873 to 423 K. Once the temperature reached 423 K, the gas stream was switched from pure H_2 to the reactant mixture (anisole/H_2 = 0.16/balance, vol %, total flow rate ∼1.67 cm^3 s^{-1}) to perform vapor phase anisole HDO under ambient pressure.

An oxygen-treated Mo_2C catalyst was prepared using a method similar to that reported by Ribeiro et al.[9,11,17] A freshly synthesized Mo_2C catalyst (from ∼1.6 g AMT), following a temperature protocol for the typical Mo_2C synthesis described above, was cooled to RT in H_2 flow (∼2.3 cm^3 s^{-1}), subsequently treated in a flow of 1% O_2/He (3.75 cm^3 s^{-1}) at RT for 2 h and thereafter at ∼423 K for 30 min (ramping rate ∼0.07 K s^{-1}). After oxygen treatment, the catalyst was quenched to RT in a flow of H_2/Ar (87.5/12.5, vol %, total flow rate ∼2.67 cm^3 s^{-1}), followed by heating at ∼723 K for 1 h with a ramping rate ∼0.12 K s^{-1} from RT (Figure S1, Table S1 in the Supporting Information (SI)), and then cooled in the same H_2/Ar mixture flow to 423 K prior to reaction rate/apparent activation energy measurements for vapor phase anisole HDO. An independent experiment was performed in which the oxygen-treated Mo_2C catalyst, after being treated in a flow of H_2/Ar (87.5/12.5, vol %, total flow rate ∼2.67 cm^3 s^{-1}) at 723 K for 1 h and cooled to RT, was subjected to a second temperature-programmed surface reaction with H_2/Ar (87.5/12.5, vol %, total flow rate ∼2.67 cm^3 s^{-1}) at 773 K for ∼5 h with a ramping rate 0.19 K s^{-1} (Figure S2, Table S1 in the SI) to assess the amount of oxygen incorporated and retained on or in the molybdenum carbide catalyst before vapor phase anisole HDO. The reactor effluent during catalyst treatments was monitored and quantified by using an online mass spectrometer with calibrated response factors.

MoO_3 (Sigma, 99.5+ % ACS Reagent) catalysts were used as received and sieved (177−400 μm) prior to kinetic measurements of vapor phase anisole HDO.

2.2. Materials Characterization. The bulk structures of the samples were characterized by X-ray diffraction with three measurement frames at 30° (2θ), 60° (2θ), and 90° (2θ) at a 600 s $frame^{-1}$ dwell (Δ2θ frame width of 35° (2θ)) (XRD, Bruker D8 Discover 2D X-ray diffractometer with a two-dimensional VÅNTEC-500 detector, Cu Kα X-ray radiation with a graphite monochromator, and a 0.5 mm point collimator). Two-dimensional images were then converted to one-dimensional intensity vs 2θ for analysis. CO chemisorption experiments were performed using a Micromeritics ASAP 2020 analyzer. An appropriate amount of sample (0.1−0.5 g) was loaded into a chemisorption cell, followed by evacuation at 383 K (∼2 μm Hg) for 0.5 h, H_2 treatment at 723 K for 2 h, and degassing (∼2 μm Hg) at 723 K for 2 h, and then cooled to 323 K. Subsequently, the first CO adsorption isotherm (total adsorbed species, between 100−450 mmHg) was measured at 323 K. The cell was then degassed (∼2 μm Hg) to remove weakly adsorbed species prior to the second isotherm. Both isotherms were extrapolated to zero pressure, and the amount of strongly adsorbed CO was obtained by the difference between the two extrapolated values.[4,18] Unless otherwise mentioned, the BET surface area measurements (Micromeritics ASAP 2020) were carried out immediately after the chemisorption measurements. The samples, after chemisorption, were passivated by flowing 1% O_2/He gas mixture for at least 0.5 h prior to being removed from the chemisorption cell and subsequently loaded in physisorption cells for N_2 adsorption experiments without any degassing pretreatments.

2.3. Steady State Kinetic Measurements of Vapor Phase Anisole HDO. A passivated Mo_2C sample (~0.25 g with CO chemisorption uptake ~79 μmol g^{-1}) was placed in a tubular quartz reactor (i.d. 10 mm) and pretreated in a pure H_2 flow (~1.67 cm^3 s^{-1}) at ~750 K for 1 h with a ramping rate ~0.125 K s^{-1} and cooled to reaction temperature ~423 K before vapor phase anisole HDO at ambient pressure.

MoO_3 samples (~0.42 g of MoO_3 per batch) were pretreated in a flow of pure H_2 (~1.67 cm^3 s^{-1}) at ~675 K for 1−6 h with a ramping rate ~0.1 K s^{-1}, instead of 750 K, prior to vapor phase anisole HDO at 423 K under ambient pressure.

Vapor phase anisole HDO reactions were carried out by feeding a reaction mixture (~1.67 cm^3 s^{-1}) consisting of ~0.15−0.75/bal (vol %) of anisole/H_2. Anisole (Sigma, 99%, ReagentPlus) was added using a syringe pump (KD Scientific, model 100). All flow lines were heated to at least 373 K via resistive heating to prevent condensation of anisole and reactor effluents. The products for anisole HDO were quantified using a flame ionization detector (FID) of a gas chromatograph (Agilent 6890 equipped with a methyl-siloxane capillary column (HP-1, 50 m × 320 μm × 0.52 μm)) with calibrated response factors. The apparent activation energy was measured after the rates had reached steady state by varying the reaction temperature between 408 to 438 K. The carbon balance was typically better than 90%. The anisole conversion and product selectivity were calculated as follows:

$$\text{anisole conversion} = \frac{(\text{sum of moles of carbon in products})_{\text{out}}}{(\text{moles of carbon in anisole})_{\text{in}}}$$

$$C_6^+ \text{ products selectivity } (C_6^+ \text{ basis}) = \frac{\text{moles of } C_6^+ \text{ product}_i}{\sum \text{moles of } C_6^+ \text{ products}}$$

$$C_1 \text{ products selectivity } (C_1 \text{ basis}) = \frac{\text{moles of methane or methanol}}{\text{moles of methane} + \text{moles of methanol}}$$

2.4. In Situ CO Titration of Mo_2C Catalysts for Vapor Phase Anisole HDO. In situ CO titration was carried out after steady state benzene synthesis rates were observed in which 0.43−8.5 g of Mo_2C (with equivalent 180−560 μmol of CO chemisorption sites in the reactor) was employed. A gas mixture of CO (~0.005 to ~0.053 cm^3 s^{-1})/Ar (~0.03 cm^3 s^{-1}) was introduced into the reactant stream (anisole/H_2 (vol %) = ~0.36 to ~0.75/bal) with a total flow rate ~1.67 cm^3 s^{-1}, which corresponds to CO partial pressures ranging from ~0.3 to ~3.1 kPa. An online mass spectrometer (MKS Cirrus 200 Quadrupole mass spectrometer system) was used to track the resulting transient response of Ar, CO, and the synthesis rates of benzene during each titration experiment. The Ar flow was used as a tracer to calculate the average residence time of CO over the catalyst bed, which was used to determine the amount of CO adsorbed and/or reacted over the surface of the Mo_2C during titration. The turnover frequency (TOF) of benzene synthesis, by assuming that one CO molecule titrates one active site, was therefore obtained (see section 3.1 for a detailed description). Replicates of CO titration experiments with the same or different CO flow rates were conducted to determine the error associated with the TOF calculation in which the reported error for TOF is a standard deviation calculated from the multiple measurements.

2.5. Transient Measurements of Vapor Phase Anisole HDO. Approximately 2.1 g of the Mo_2C catalyst with CO chemisorption uptake ~199 μmol g^{-1} was loaded into a reactor and pretreated in pure H_2 (~1.67 cm^3 s^{-1}) at ~723 K for 1 h (~0.12 K s^{-1}), followed by cooling the sample in the H_2 flow to ~423 K prior to the introduction of a reaction mixture consisting of ~0.75/16.7/bal (vol %) of anisole/Ar/H_2 (total flow rate ~2 cm^3 s^{-1}). Ar, cofed in the reaction feed, served as an internal standard for quantification of the reactor effluents during transient measurements using a mass spectrometer (MKS Cirrus 200 Quadrupole MS system). The reaction reached steady state after ~6 ks time-on-stream (Figure S3 in the SI). A mass balance of oxygen-containing species (anisole, methanol, water, CO and CO_2) from 0 to 6 ks or carbon species from 0 to 8 ks was used to assess the amount of oxygen or carbon accumulated on/in the Mo_2C catalyst during this transient. All transient kinetic measurements were conducted at anisole chemical conversions <20%.

2.6. Temperature-Programmed Surface Reaction with H_2 (TPSR) Study of Mo_2C Catalysts after Anisole HDO. A temperature-programmed surface reaction with H_2 (TPSR) was performed on the Mo_2C sample used for transient kinetic analysis (section 2.5) after ~43 ks in vapor phase anisole HDO at 423 K under ambient pressure (Figure S3 in the SI). The feed was first switched from the reaction mixture consisting of 0.75/16.7/bal (vol %) of anisole/Ar/H_2 (total flow rate ~2 cm^3 s^{-1}) to pure He (total flow rate ~5 cm^3 s^{-1}) for 0.72 ks to remove weakly bound surface species at ~423 K; subsequently, the feed was switched to a H_2/Ar mixture (83.3/16.7, vol %, ~2 cm^3 s^{-1}) for 0.3 ks, followed by heating the sample from 423 to 730 K at a ramping rate of ~0.17 K s^{-1}. The reactor effluents were monitored and quantified (using Ar as an internal standard) using a mass spectrometer.

3. RESULTS AND DISCUSSION

3.1. In Situ CO Titration of Mo_2C Catalysts for Vapor Phase Anisole HDO. Molybdenum carbide catalysts were first allowed to reach steady state for vapor phase anisole HDO prior to introducing a CO/Ar cofeed (section 2.4). Benzene synthesis rates were found to be significantly suppressed in the presence of CO, but they could be fully restored upon the removal of CO, suggesting that CO is a reversible titrant, as shown in Figure 1. Multiple CO titration experiments with different CO flow rates (~0.005 to ~0.028 cm^3 s^{-1}) were then performed to obtain the TOF of benzene synthesis per CO chemisorption site. Figure 2 shows the mass spectrometer signals of benzene, CO, and Ar as a function of time during a typical CO titration experiment. Since a synchronic breakthrough of both Ar and CO mass spectrometer signals was observed in a blank experiment in which CO (0.005−0.025 cm^3 s^{-1})/Ar (0.033 cm^3 s^{-1}) gas mixtures were cofed in an empty reactor with pure H_2 gas flow (1.67 cm^3 s^{-1}) (Figure S4 in the SI), the apparent residence time of CO in the reactor (the delayed breakthrough time for CO as compared with that of Ar)

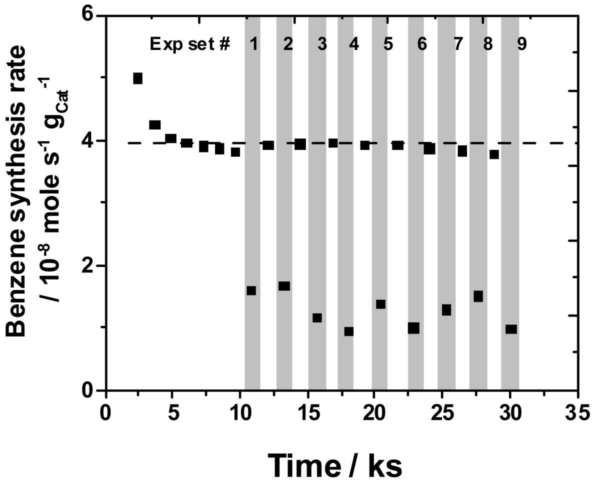

Figure 1. Benzene synthesis rates vs time-on-stream during the course of in situ CO titration. The catalyst (~1.11 g, CO chemisorption uptake ~240 μmol g^{-1}) was stabilized for ~10 ks before in situ CO titration. Shaded areas indicate CO/Ar mixtures (~0.005 to ~0.028 cm^3 s^{-1}/~0.036 cm^3 s^{-1}) were cofed into the reactant feed comprising anisole/H_2 (vol %) = ~0.36/bal with a total flow rate ~1.67 cm^3 s^{-1} at reaction temperature ~423 K under ambient pressure. The dashed line is shown as a guide to the eye.

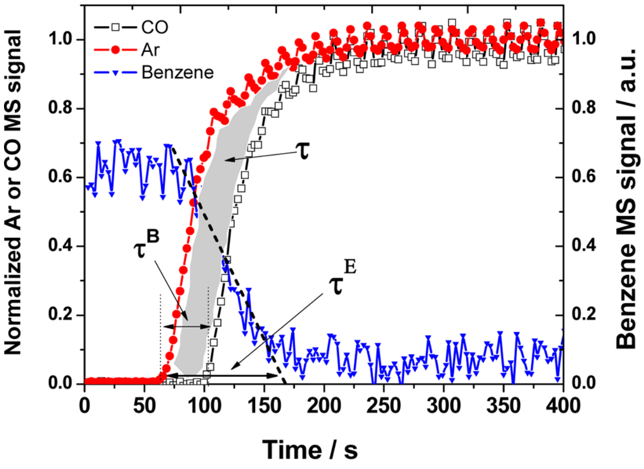

Figure 2. Normalized Ar (m/z = 40), CO (m/z =28) and benzene mass spectrometer signals (m/z = 78, corrected by subtracting the signal contributed from anisole) during the course of in situ CO titration. τ^B, τ, and τ^E, represent the breakthrough time of CO, average residence time of CO determined by integration of the normalized Ar and CO breakthrough curves (shaded area) and extrapolated residence time of CO, which was used to calculate the amount of CO required to shut down benzene synthesis (see section 3.1). CO/Ar was cofed as a titrant/inert tracer with a flow rate of ~0.0126 cm^3 s^{-1}/~0.036 cm^3 s^{-1} into a reactant feed comprising anisole/H_2 (vol %) = ~0.36/bal (total flow rate ~1.67 cm^3 s^{-1}) at a reaction temperature ~423 K under ambient pressure; Mo_2C loading ~1.11 g (CO chemisorption 240 μmol g^{-1}). Benzene synthesis rates in the presence/absence of CO were measured by GC before 0 s and after 400 s.

was attributed to adsorption or reactions (CO hydrogenation and/or water gas shift) over the catalysts.

The number of active sites occupied by CO can be estimated by multiplying the known CO molar flow rate and the CO residence time (τ^B, the difference of the breakthrough times between the CO and Ar signals) if we consider that CO hydrogenation or CO consumed via the water gas shift contributes negligibly to the observed CO residence time, which will be discussed later. Alternatively, the average residence time of CO, τ, can be estimated by calculating the area between the Ar and CO curves as shown in Figure 2 in which both Ar and CO signals were normalized to their corresponding values obtained at steady state.[19] The number of CO molecules adsorbed on the molybdenum carbide catalyst could be obtained by multiplying the average CO residence time and the known CO molar flow rate. The residence times of CO obtained by the two different methods outlined above were found to be in agreement (with error typically <15%), as shown in Table 1. The TOF of benzene synthesis per metallic site on molybdenum carbide catalysts (with the assumption that one CO molecule poisons one active site for benzene synthesis) can therefore be rigorously calculated on the basis of the ratio of the reduction of benzene synthesis rate due to the presence of CO and the amount of CO adsorbed on the catalyst. The resulting values were found to be $1.1 \pm 0.3 \times 10^{-3}$ mol s^{-1} mol_{COsite}^{-1} (Table 1). Nearly invariant benzene TOF values with different CO flow rates ranging from 0.005 to 0.053 cm^3 s^{-1} were also obtained, as shown in Figure 3 (the detailed data for the three sets of titration experiments used to plot Figure 3 can be found in Table 1 and Tables S2, S3 in the SI), suggesting (i) the absence of CO mass transfer limitations during the in situ titration, (ii) a negligible effect of CO hydrogenation on the TOF calculation, and (iii) little or no diversity in the active sites titrated by CO under conditions employed in this work. The number of operating active sites obtained via (benzene synthesis rates in the absence of CO)/(measured TOF) was found to be 34 ± 7 μmol g^{-1} (average value shown in Table 1 with catalyst loading 1.11 g), which corresponds to ~13% of the total potential active sites measured by ex situ CO chemisorption (~240 μmol g^{-1}).

Since molybdenum carbide catalysts have been shown to be active for CO hydrogenation and water gas shift,[6−8,20] the observed average CO residence time (τ in Figure 2) can be contributed from both CO competitive adsorption with anisole on active sites for HDO and CO adsorption/reaction on sites active for CO hydrogenation or water gas shift. No detectable amount of CO_2 was observed (TCD, with He as the GC carrier gas) during in situ CO titration, suggesting that the effect of the water gas shift on the estimation of CO adsorption sites can be neglected.

The molar ratio between C_1 and C_6 species during vapor phase anisole HDO (1 atm and 423 K) was found to be stoichiometric (C_1/C_6 ~1), as shown in our previous report.[3] The observed excess in stoichiometric values of C_1 formation rates (i.e., relative to benzene synthesis rates) must therefore come from CO hydrogenation (Table 1). Shou and Davis[20] employed steady-state isotopic transient kinetic analysis to assess the number of active intermediates (i.e., operating active sites) over supported Mo_2C catalysts and concluded that <1% of the surface Mo sites were involved in CO hydrogenation reactions at 573 K under 1.2 bar with a CO/H_2 molar ratio = 1. We note that although the coverage of active intermediates for CO hydrogenation at our reaction temperature (423 K) is expected to be higher, the much lower CO partial pressure (<2 kPa) employed during in situ CO titration experiments would have a counter effect on the coverage. The contribution of CO adsorption associated with hydrogenation to the observed average CO residence time (τ) is, therefore, assumed to be negligible.

The amount of CO required to completely deactivate vapor phase anisole HDO rates (i.e., the number of operating sites) can also be obtained by multiplying the known CO flow rate and the

Table 1. Experimental Conditions and Measured Kinetics for in Situ CO Titration of Mo_2C Catalysts with Catalyst Loading ~1.11 g[a] in Vapor Phase Anisole HDO shown in Figures 1, 3, and 7

exptl set	cond	benzene rate (× 10^{-8} mol s^{-1})[b]	methane rate (× 10^{-8} mole s^{-1})[b]	methanol rate (× 10^{-8} mole s^{-1})[b]	CO mol flow rate (× 10^{-6} mol s^{-1})	avg CO residence time τ (s)[c]	apparent amt CO adsorbed (× 10^{-5} mol)[d]	TOF (10^{-3} mol s^{-1} mol_{COsite}^{-1})[e]	TOF based on extrapolation (mol s^{-1} mol_{COsite}^{-1})[f]	no. of operating sites during anisole HDO reaction (μmol)[g]
1	no CO	4.3	0.8	3.8						
	with CO	1.8	1.3	4.2	0.3	68 (54)	2.1	1.2	1.3	32
2	no CO	4.4	0.8	3.9						
	with CO	1.9	1.3	4.3	0.3	54 (48)	1.7	1.5	1.4	26
3	no CO	4.4	0.8	3.5						
	with CO	1.3	1.8	4.7	1.0	27 (23)	2.8	1.1	0.7	37
4	no CO	4.4	0.9	3.6						
	with CO	1.1	2.2	4.6	2.1	16 (17)	3.4	1.0	0.4	43
5	no CO	4.4	0.9	3.8						
	with CO	1.5	1.6	4.1	0.5	35 (37)	1.8	1.6	1.1	25
6	no CO	4.4	0.9	3.4						
	with CO	1.1	2.0	4.6	1.5	20 (20)	3.1	1.0	0.5	40
7	no CO	4.3	0.9	3.5						
	with CO	1.4	1.7	4.1	0.7	31 (20)	2.2	1.3	0.8	31
8	no CO	4.3	0.9	3.6						
	with CO	1.7	1.5	4.0	0.4	45 (43)	1.8	1.4	1.4	28
9	no CO	4.2	0.9	3.5						
	with CO	1.1	2.0	4.1	1.7	19 (23)	3.3	0.9	0.5	44

[a] CO chemisorption uptake ~ 240 μmol g^{-1}. [b] Reaction conditions: anisole/H_2 (vol %) = ~0.36%/bal with total flow rate ~1.67 cm^3 s^{-1} at reaction temperature ~423 K, anisole conversion and benzene selectivities (steady state values in the absence of CO) during the course of titration were ~19% and ~95% respectively. [c] Obtained by integrating the area between normalized Ar and CO signals as shown in Figure 2; the number in the parentheses represents the CO breakthrough time in seconds (τ^B as shown in Figure 2). [d] Obtained via multiplying CO molar flow rate by average CO residence time. [e] Obtained by ((benzene rates without CO) − (benzene rates with CO))/(apparent amount of CO adsorbed on the catalysts during CO titration). [f] Obtained by extrapolation method; see section 3.1 for detailed information. [g] Obtained by (benzene rates without CO)/(the corresponding measured TOF).

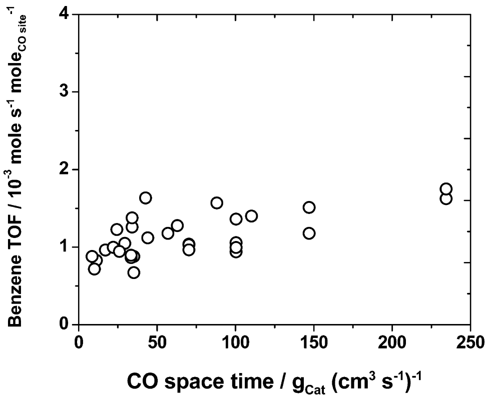

Figure 3. Turnover frequency (TOF) of benzene synthesis determined by in situ CO titration as a function of CO space time, defined as (amount of catalyst)/(CO cofeed flow rate employed in the corresponding titration experiments). Different CO space times were achieved using both different amounts of catalyst (~1.77, ~1.11, ~0.43 g) and different CO cofed flow rates (~0.0076−0.053 cm^3 s^{-1}). Data shown in Tables 1, S2, and S3 were used to plot this figure. Reaction conditions: feed composition, anisole/H_2 (vol %) = 0.36−0.75/bal; reaction temperature, 423 K; ambient pressure; anisole conversion ~10 to ~19% with benzene selectivity ~95%.

CO residence time obtained by linearly extrapolating the initial slope of the benzene synthesis rates to zero[21] by assuming that (i) CO adsorption is irreversible and far away from equilibrium at low CO coverage and (ii) all active sites behave the same in the linear regime, as demonstrated in Figure 2. The TOF can therefore be calculated on the basis of the ratio of observed benzene synthesis rates in the absence of CO and the measured amount of operating sites determined via the extrapolation method. No significant difference was found in the TOF values obtained from the two different methods as shown in Table 1, which suggests that the lag of the CO breakthrough curve relative to Ar (Figure 2) was dominated by CO competitive adsorption with anisole on the active sites for HDO, not on the sites for CO hydrogenation.

3.2. Transient Kinetic Measurements of Vapor Phase Anisole HDO over Molybdenum Carbide Catalysts. An oxygen mass balance during the transient of anisole HDO and a temperature-programmed surface reaction with H_2 of a sample after being tested for ~43 ks for anisole HDO (section 3.3) were performed to examine the extent of in situ oxidation of molybdenum carbide catalysts by anisole during HDO at 423 K under ambient pressure with a high H_2 to anisole ratio (~110) in the reactant feed. Figure 4a shows mass spectrometer signals of anisole and the corresponding products as a function of time during the transient (<6 ks) in which time zero indicates the

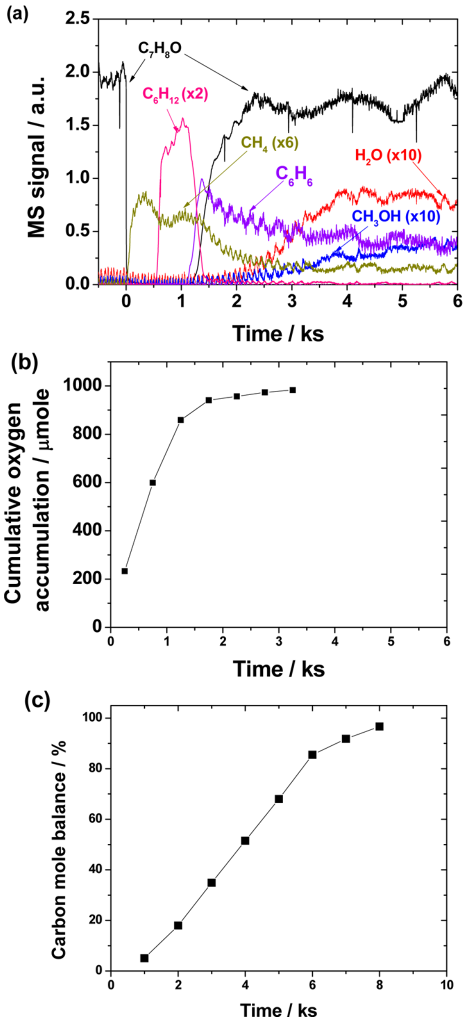

Figure 4. (a) Transient mass spectrometer (MS) signals of benzene (C_6H_6, $m/z = 78$, corrected by subtracting the signal contributed from anisole), anisole (C_7H_8O, $m/z = 108$), cyclohexane (C_6H_{12}, $m/z = 84$), methane (CH_4, $m/z = 16$), methanol (CH_3OH, $m/z = 31$), and water (H_2O, $m/z = 18$) for 2.1 g of Mo_2C (BET surface area ~ 96 $m^2\ g^{-1}$, CO chemisorption ~ 199 μmol g^{-1}) tested in the vapor phase anisole HDO reaction at ~423 K under ambient pressure with reaction feed composition: anisole/Ar/H_2 (vol %) = 0.75/16.7/bal (total flow rate ~ 2 $cm^3\ s^{-1}$); (b) cumulative oxygen accumulation in the Mo_2C catalyst obtained by calculating an oxygen mole balance (considering only H_2O, CH_3OH, C_7H_8O) every 0.5 ks from 0 to 3.5 ks, during the transient of anisole HDO shown in part (a); (c) carbon mole balance during the transient of anisole HDO shown in part (a). Each data point represents the carbon mole balance starting from 0 ks time-on-stream. Carbon mole balance was defined as (mole of carbon measured at the outlet)/(mole of anisole fed in × 7).

switch of the reactant feed from bypass to the reactor. Upon the introduction of the reaction feed, methane was observed immediately, followed by cyclohexane at time-on-stream ~0.5 ks. No oxygen-containing products (water and methanol) were observed before ~1.5 ks, suggesting that oxygen accumulation (in situ oxidation of the molybdenum carbide catalyst) occurred prior to steady state rates of anisole HDO being attained. Benzene was found to increase at the expense of cyclohexane, with a concurrent increase in oxygen-containing products, water and methanol, at time-on-stream ~1.2 ks. The presence of oxygen in molybdenum carbide catalysts was previously shown to significantly suppress hydrogenation of benzene to cyclohexane in independent studies.[3,13,14] The observation of cyclohexane prior to benzene formation shown in Figure 4a can therefore be explained via sequential hydrogenation of benzene to cyclohexane by the catalyst that is not yet oxidized.

Figure 4b shows the cumulative oxygen accumulation as a function of time, calculated by performing an oxygen mass balance (considering anisole, water, and methanol as the only oxygen-containing species) every 500 s (between 0 and 3.5 ks). The total oxygen retained in the molybdenum carbide catalyst, after ~3.5 ks as shown in Figure 4b, was found to be ~982 μmol (~468 μmol g^{-1}), which corresponds to ~0.29 monolayer of oxygen, on the basis of the measured BET surface area of the sample ~96 $m^2\ g^{-1}$ (BET surface area was obtained from an independent experiment before vapor phase anisole HDO) and a Mo site density of 1×10^{15} sites cm^{-2} (Table 2).[14] The observed in situ oxidation of molybdenum carbide during HDO is similar to that reported by Prasomsri et al.[22] in which the authors concluded that the surface of MoO_3 can be partially carburized during HDO to generate oxycarbide or oxycarbohydride phases, as evidenced by XPS (observation of Mo^{5+} species) and XRD (observation of oxycarbohydride phase).

Figure 4c shows the calculated carbon mass balance as a function of time during the transient, for which only anisole, benzene, cyclohexane, methane, and methanol were considered. The time required for the carbon balance to close (~8 ks) was found to be longer than that for the oxygen balance (~4 ks). Carbon accumulation between 0 and 8 ks time-on-stream was found to be ~8100 μmol g^{-1} (equivalent to ~1350 μmol g^{-1} of C_6 species), which corresponds to C_1 and C_6 species coverage of ~510% and ~85%, respectively, on the basis of a BET surface area of 96 $m^2\ g^{-1}$ and a Mo site density of 1×10^{15} sites cm^{-2} (Table 2).[14] The carbon mass balance suggests that carbon deposition also occurred in the transient (before ~8 ks) prior to steady state rates for vapor phase anisole HDO being attained; C_1 species are inferred to be preferentially deposited on the surface of molybdenum carbide catalysts because the calculated C_1/C_6 molar ratio was significantly less than 1 during this time period, as shown in Figure S5.

3.3. Temperature-Programmed Surface Reaction with H_2 of Spent Molybdenum Carbide Catalysts.

A temperature-programmed surface reaction with H_2 of the molybdenum carbide catalyst tested for anisole HDO for 43 ks (the same sample used for the transient kinetic study discussed in section 3.2 and shown in Figure S3 in the SI) was directly performed (without exposure to air) to determine the amount of oxygen accumulated during the transient of the vapor phase anisole HDO; the data are shown in Figure 5. Benzene (mass spectrometer signal, $m/z = 78$) was observed upon switching the gas flow from pure He to the H_2/Ar gas mixture. This observation supports the reaction mechanism proposed in our previous work wherein anisole decomposes to form C_6H_5 intermediates that can desorb from the surface only by reaction with H* species derived from molecular H_2 and in the absence of H_2 persist on the surface.[3] After purging the catalyst in a flow of H_2/Ar for ~0.3 ks, the temperature was ramped to 730 K at a ramping rate 0.17 K s^{-1}, and both oxygen-containing species (water, methanol, CO and CO_2) and carbon species (C_1: CO, CO_2, methane, and methanol; C_6: benzene, cyclohexane, and anisole) were observed during the temperature ramp. Benzene evolution occurred at earlier times-on-stream (~1.2 ks) than oxygen-containing species (except for methanol), which suggests that most of the oxygen in the molybdenum carbide catalyst could not be removed at ~420 K, and consequently, the

Table 2. Amount of Oxygen and Carbon Species Retained on/in the Mo_2C Catalyst during the Transient of Vapor Phase Anisole HDO as Shown in Figure 4

cat. amt (g)	BET surface area[a] (m^2 g^{-1})	CO chemisorption uptake[b] (323 K, μmol g^{-1})	oxygen coverage[c] (%)	equiv C_6 coverage[d] (%)	oxygen coverage obtained by TPSR[e] (%)	C_6 coverage obtained by TPSR[f] (%)
2.1	96	199	29	85	25	14 (110)

[a] No H_2 pretreatment was performed prior to the BET measurement. [b] Average value of two independent CO chemisorption measurements: 204 and 194 μmol g^{-1}. [c] Oxygen accumulation (water, methanol, and anisole were considered) during the transient of vapor phase anisole HDO shown in Figure 4a. Oxygen accumulation between 0 and 3.5 ks time-on-stream (Figure 4b) was found to be ∼468 μmol g^{-1}. Oxygen coverage was calculated based on a site density of $\sim 1 \times 10^{15}$ sites cm^{-2} and the measured BET surface area, ∼96 m^2 g^{-1}. [d] Carbon accumulation (only methane, methanol, benzene, cyclohexane, and anisole were considered) between 0 and 8 ks time-on-stream (Figure 4c) was found to be ∼8100 μmol g^{-1}, which is equivalent to ∼1350 μmol of C_6 per gram of catalyst. C_6 coverage was calculated on the basis of the assumption described in footnote c, above. [e] Amount of oxygen-containing species (water, methanol, anisole, CO, and CO_2 were considered) measured during the TPSR experiment shown in Figure 5 was found to be ∼402 μmol g^{-1}. Oxygen coverage was calculated on the basis of the assumption described in footnote c, above. [f] Amount of carbon (methane, methanol, CO,CO_2, benzene, cyclohexane and anisole were considered) measured during the TPSR experiment shown in Figure 5 was found to be ∼1655 μmol g^{-1}. The amount of C_6 species, including benzene, cyclohexane, and anisole, was found to be ∼225 μmol g^{-1}, which is used to calculate the surface C_6 species coverage on the basis of the assumption described in footnote c, above. The number in parentheses represents the C_6 coverage on the basis of CO chemisorption uptake measured at 323 K shown in this table.

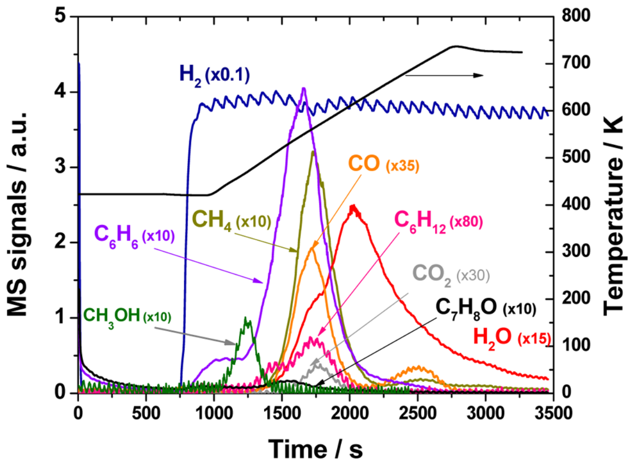

Figure 5. Temperature-programmed surface reaction with H_2 (TPSR) of the Mo_2C catalyst after being tested in vapor phase anisole HDO for ∼43 ks, as shown in Figure S3. The catalyst was purged in a flow of He (∼5 cm^3 s^{-1}) at ∼423 K for ∼720 s, followed by switching the gas from He to H_2/Ar (= 83.3/16.7, vol %, total flow rate ∼2 cm^3 s^{-1}) gas mixture at ∼423 K for ∼300 s; subsequently, the temperature was ramped from ∼423 to ∼730 K with a ramp rate ∼0.17 K s^{-1}. The MS signal of m/z = 78 was directly assigned to benzene because the contribution from anisole was negligible.

sequential hydrogenation of benzene to cyclohexane was significantly inhibited before ∼1.2 ks (∼420 K). Once oxygen-removal in the molybdenum carbide catalyst started (∼1.5 ks, corresponding to ∼460 K in Figure 5), a notable increase in cyclohexane formation was observed concurrently, as expected. Quantification of the amount of oxygen retained in the molybdenum carbide (only water, methanol, anisole, CO, and CO_2 were considered) during the TPSR experiment gave ∼0.25 monolayer of oxygen based on a BET surface area of 96 m^2 g^{-1} and a Mo site density of 1×10^{15} sites cm^{-2} (Table 2)[14], which (i) is in agreement with the value obtained from the oxygen balance during the transient of anisole HDO (∼0.29 monolayer) shown in Figure 4 and confirms in situ oxidation of molybdenum carbide during vapor phase anisole HDO and (ii) suggests negligible further oxidation of the molybdenum carbide catalyst occurred during steady state vapor phase anisole HDO.

The amount of carbon evolved during the TPSR experiment was found to be ∼1655 μmol g^{-1} (Table 2), which is significantly lower than that obtained from the carbon balance during the transient of vapor phase anisole HDO (∼8100 μmol g^{-1}), suggesting that some residual carbonaceous species were retained on the catalyst and could not be removed upon the thermal treatment in H_2 to ∼730 K. This mild coke formation, in addition to in situ oxidation of molybdenum carbide catalysts by anisole, could cause the initial deactivation of benzene synthesis rates (<3 ks shown in Figure S3 in the SI), Three different types of carbonaceous species—near surface carbide, polymeric, and graphitic carbon—inherited from different carburization conditions during molybdenum carbide synthesis, have been identified and found to be removed as CH_4 at temperatures ∼763, ∼963 K, and ∼1083 K, respectively, during temperature-programmed surface reaction with H_2 (TPSR) by Oyama and coworkers,[23] which suggests the difficulty of removing carbonaceous species. C_6 species (only benzene, cyclohexane, and anisole were considered) eluted from the reactor during the TPSR experiment (Figure 5) were found to be ∼225 μmol g^{-1}, which corresponds to ∼110% coverage on the basis of the total number of potential active sites as assessed by ex situ CO chemisorption at 323 K (199 μmol g^{-1}), implying that C_6 species are potentially the dominant surface species, consistent with the observed zero-order dependence in anisole pressure of HDO rates reported previously.[3]

3.4. Temperature-Programmed Surface Reaction with H_2 of Passivated Mo_2C Catalysts.

Figure 6 shows the

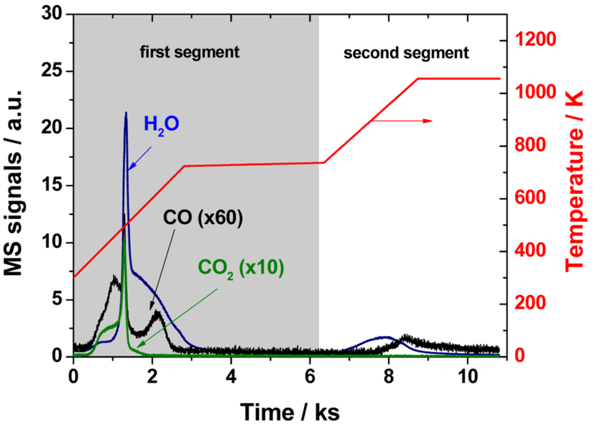

Figure 6. Temperature-programmed surface reaction with H_2 (TPSR) of the passivated Mo_2C catalyst with CO chemisorption uptake ∼79 μmol g^{-1}, in which two consecutive segments (shaded region (RT to 723 K) and unshaded regions (723 to 1056 K), heating rate ∼0.16 K s^{-1}) were employed. Catalyst loading ∼0.25 g; H_2 flow = 1.67 cm^3 s^{-1}.

Table 3. Quantification of Water Evolved during Temperature Programmed Surface Reaction with H_2 of the Passivated Mo_2C Catalyst Shown in Figure 6 and the Corresponding Benzene Synthesis Rates/Selectivity for Vapor Phase Anisole HDO at 423 K at 1 atm

temp protocol[a]	H_2O removed in 1st segment of TPSR (μmol g^{-1})[b]	H_2O removed in 2nd segment of TPSR (μmol g^{-1})[c]	BET surf area (m^2 g^{-1})[d]	CO chemisorption uptake (μmol g^{-1})[e]	oxygen coverage after 1st segment of TPSR (monolayer)[f]	cat. formulation after 1st segment of TPSR[g]	benzene synthesis rate ($\times 10^{-8}$ mol s^{-1} g^{-1})[h]	benzene sel. (%)[h]
RT (45 min)−723 K (1 h)−1056 K (40 min) (0.5 h)	5988	1416	64	79	1.3	$Mo_2CO_{0.3}$	3.2 (4.0×10^{-4})	90

[a] See section 2.1 for the nomenclature of the temperature protocols. Catalyst loading: ~0.25 g. [b] Amount of water removed during a typical catalyst activation process employed in this work (the first segment of the temperature protocol, indicated as the shaded region shown in Figure 6). [c] Amount of water removed during the second segment of the TPSR experiment, as shown in Figure 6. [d] Obtained by using the sample right after CO chemisorption measurement; the sample was passivated by 1% O_2/He prior to BET measurement. [e] Obtained by an independent measurement in which the sample was pretreated in H_2 at 723 K for 2 h prior to the CO chemisorption measurement at 323 K. [f] CO and CO_2 shown in Figure 6 were not included for calculating the oxygen coverage. BET surface area (64 m^2 g^{-1}) and a Mo site density (~1×10^{15} sites cm^{-2}) were used to calculate the oxygen coverage. [g] CO and CO_2 shown in Figure 6 were not included for the catalyst formulation calculation. Mo_2CO_y was used to estimate the stoichiometry of the catalyst formulation by assuming that all of the oxygen was removed after the second segment of the TPSR experiment (see SI for detailed information). [h] Reaction was carried out at ~423 K under ambient pressure with reaction feed comprising anisole/H_2 (vol %) = 0.16/bal (total flow rate ~1.67 cm^3 s^{-1}). The number in parentheses represents benzene synthesis rates per CO chemisorption site. Data reported as an average value of 1−2 h time-on-stream, and the corresponding benzene synthesis rate/benzene selectivity vs time-on-stream is shown in Figure S6.

temperature-programmed surface reaction with H_2 (TPSR) of a representative passivated molybdenum carbide catalyst in which the benzene synthesis rate per CO chemisorption site (by ex situ CO chemisorption at 323 K), ~4×10^{-4} mol s^{-1} mol_{COsite}^{-1} (Table 3), was found to be within the average value of those reported previously (average value $3.4 \pm 1.0 \times 10^{-4}$ mol s^{-1} mol_{COsite}^{-1});[3] the corresponding benzene synthesis rate as a function of time is shown in Figure S6. The temperature profile consisted of two consecutive segments in which the first one was intended to simulate the typical catalyst activation process (catalysts treated in a flow of H_2 at ~723 K for 1 h; see section 2.3), and the second segment attempted to remove the residual oxygen, if any, in the molybdenum carbide catalysts via a temperature ramp to 1056 K. Oxygen was found to be removed predominantly in the form of water (~7400 μmol g^{-1}, Table 3), which is at least ~20 times in excess of the amount removed as CO (~150 μmol g^{-1}) or CO_2 (~340 μmol g^{-1}) during the entire TPSR process (Figure 6).

The observed water profile shown in Figure 6 is similar to that reported by Leary et al.[24] in which a sharp water peak was observed at 518 K, followed by two close peaks at 598 and 658 K. Quantification of the amount of oxygen evolved during the TPSR experiment, in which water was considered as the only oxygen-containing eluent, revealed that only ~81% of oxygen in the passivated molybdenum carbide catalyst could be removed during the typical activation process (H_2 treatment at 723 K for 1 h, the first segment shown in Figure 6) if we assume that 100% oxygen removal can be achieved at 1056 K in the presence of H_2 flow. This experimental observation is in line with the difficulty of completely removing oxygen in tungsten carbide catalysts reported by Ribeiro et al.[18] in which 50% of oxygen was found to be still retained after thermal treatment in H_2 at 1150 K. The BET surface area of this molybdenum carbide sample was found to be ~64 m^2 g^{-1} (after CO chemisorption as described in section 2.2). The amount of oxygen retained in a molybdenum carbide catalyst after the typical activation process (segment A, Figure 6) was found to be ~1.3 monolayers on the basis of BET surface area and a surface Mo site density of 1×10^{15} sites cm^{-2},[14] which corresponds to a formulation of $Mo_2CO_{0.3}$ if (i) no excess carbon in the original molybdenum carbide is considered and (ii) 100% oxygen removal after the whole TPSR process (Table 3; see SI for the estimation of the catalyst formulation). This experimental result suggests that oxycarbidic sites exist during vapor phase anisole HDO because (i) more than one monolayer of oxygen is retained in the molybdenum carbide catalyst after H_2 treatment at ~723 K for 1 h prior to reaction, and (ii) the catalyst can be further oxidized by the reactant at 423 K, even at a high H_2-to-anisole molar ratio (~110) under ambient pressure.

3.5. Effect of Oxygen Treatment of Molybdenum Carbide Catalysts on Vapor Phase Anisole HDO.

Iglesia et al.[8,25] have shown that oxygen treatment can significantly increase the isomerization selectivity of *n*-hexane (from 0 to 99%) at 520 K, which was attributed to the formation of acidic sites, generated via oxygen incorporation, in tungsten carbide catalysts. Oxygen treatment has also been shown to suppress hydrogenolysis and promote the isomerization of *n*-hexane over molybdenum carbide catalysts.[5] Molybdenum carbide catalysts prepared at higher carburization temperatures were found to have a higher density of CO chemisorption sites and a higher turnover frequency per CO chemisorption site for benzene hydrogenation,[13] indicating that the presence of oxygen in molybdenum carbide catalysts can simultaneously affect both the number and reactivity of the active sites (i.e., different TOF) for a given reaction.

Freshly prepared molybdenum carbide, without exposure to air, was subjected to oxygen treatment (section 2.1) to further investigate the effects of oxygen incorporation in molybdenum carbide on the kinetics of vapor phase anisole HDO. The results presented in Table 4 show a ~3 fold reduction in benzene synthesis rates per gram of catalyst for an oxygen-treated sample (2.4×10^{-8} mol s^{-1} g^{-1}) compared with a freshly prepared catalyst (6.8×10^{-8} mol s^{-1} g^{-1}). We note that the reported benzene synthesis rates per gram catalyst for both freshly prepared and oxygen-treated samples were normalized by the weight of the spent catalyst in which the catalysts were passivated in a flow of 1% O_2/He before being removed from the reactor. The weights of the spent catalysts were found to be within 3% of the theoretical weight of Mo_2C (based on AMT amount), indicating that bulk carburization of the precursor (AMT) was complete.

The presence of oxygen in the oxygen-treated molybdenum carbide sample could be inferred from the suppressed rate of cyclohexane formation during the transient of vapor phase anisole HDO as compared with that for a freshly prepared

Table 4. Vapor Phase Anisole HDO over Oxygen-Treated and Freshly Prepared (without exposure to air) Molybdenum Carbide Catalysts at 423 K under Ambient Pressure

measured kinetics	fresh Mo_2C	oxygen-treated Mo_2C
benzene synthesis rate (mol $s^{-1}g^{-1}$)[a]	6.8×10^{-8}	2.4×10^{-8}
benzene TOF (mol s^{-1} $mol_{COsite}{}^{-1}$)[b]	1.7×10^{-3}	1.5×10^{-3}
benzene selectivity (%)	96.7	92.7
cyclohexane selectivity (%)	3.1	4.5
phenol selectivity (%)	0.2	2.0
methane selectivity (%)	11.3	20.5
methanol selectivity (%)	88.7	79.5
apparent activation energy, E_a (kJ mol^{-1})[c]	71 ± 1	65 ± 1

[a] Steady state values taken as an average of 3−4 h time on-stream. The rate per gram catalyst was normalized by the weight of the spent catalyst in which the catalyst was passivated in 1% O_2/He before being removed from the reactor. Catalysts were prepared starting from ~1.6 g AMT. [b] An average value of two independent CO titration experiments in which CO (0.035 cm^3 s^{-1})/Ar (0.035 cm^3 s^{-1}) gas mixtures were co-fed in the reactant feed; the effect of CO hydrogenation was not considered for benzene TOF calculation. [c] The corresponding Arrhenius plot is shown in Figure S8 in the SI.

molybdenum carbide catalyst (Figure S7 in the SI). The amount of oxygen incorporated in the oxygen treated molybdenum carbide samples, based on the water evolved during the TPSR experiments for the two oxygen treated Mo_2C samples (section 2.1, Table S1 in the SI), was assessed to be ~734 μmol g^{-1} (equivalent to 0.075 O/Mo_{bulk} (molar ratio)). We note that the amount of water evolved during the H_2/Ar treatment at 723 K for 1 h was found to be essentially the same, with an error of <1%, for the two oxygen-treated Mo_2C samples (Table S1 in the SI), suggesting that the oxygen treatment was reproducible and the quantification of the oxygen incorporated in the Mo_2C catalysts was representative. The TOF of benzene synthesis considering one incorporated oxygen atom to occupy one active site for anisole HDO was found to be 6×10^{-5} mol s^{-1} $mol_{Osite}{}^{-1}$. This TOF value is ~16 times lower than that obtained with CO as a titrant ($1.1 \pm 0.3 \times 10^{-3}$ mol s^{-1} $mol_{COsite}{}^{-1}$, Table 1), suggesting that oxygen can either adsorb on sites that are not related to anisole HDO chemistry or incorporate into the bulk structure of molybdenum carbide, resulting in a much higher uptake of oxygen compared with that of CO.[16,25] Oyama and co-workers have also shown that oxygen chemisorption uptake was ~6 times higher than CO chemisorption uptake on Mo_2C catalysts, resulting in a much lower turnover rate per oxygen chemisorption site for cumene hydrogenation as compared with that per CO chemisorption site.[26] CO chemisorption uptake is, therefore, a more relevant descriptor to gauge benzene synthesis rates of molybdenum carbide catalysts for vapor phase anisole HDO.

The benzene selectivity, however, was found to be similar, on both oxygen -treated and freshly prepared molybdenum carbide catalysts, at a level of ~90% on a C_6^+ basis (Table 4). No significant difference in methane/methanol selectivities was observed for the two samples, either. The apparent activation energy for benzene formation was found to be similar for both samples, ~70 kJ mol^{-1} (Table 4, and Figure S8 in the SI for the corresponding Arrhenius plot). The similarity in product selectivity as well as apparent activation energy suggests that the effect of incorporated oxygen in molybdenum carbide catalysts is to reduce the number of active sites for benzene synthesis. The unperturbed chemistry per operating site in the oxygen-treated molybdenum carbide catalysts was further evidenced by the similar benzene TOF obtained by in situ CO titration for the two samples (~1.5×10^{-3} mol s^{-1} $mol_{COsite}{}^{-1}$, Table 4). These experimental results show that although oxygen treatment can successfully introduce oxygen in a molybdenum carbide catalyst, the presence of oxygen, at least at the level of 734 μmol g^{-1} (0.075 O/Mo_{bulk} (molar ratio)), alters the number and not the identity or reactivity of the active sites for the HDO reaction.

During the transient, the fresh Mo_2C formulation can accomplish both Ar−O bond hydrogenolysis and benzene hydrogenation, as shown in Figure 4a; however, at steady state, the working catalyst that incorporates a certain amount of oxygen primarily accomplishes only Ar−O bond cleavage reactions. We cannot probe the reactivity of fresh Mo_2C samples when oxygen is present in one of the reactants and, hence, emphasize the point that oxygen accumulation after the initial transient changes only the number of sites and not their identity.

We have previously reported that CO chemisorption uptake for molybdenum carbide catalysts decreases as a function of aging time on the shelf, presumably as a result of slow oxidation via inevitable air exposure (Figure S9 in the SI).[27] Figure 7 shows that benzene synthesis TOF measured by in situ CO titration (1.1 ± 0.3 x10^{-3} mol s^{-1} $mol_{COsite}{}^{-1}$) is invariant over a series of molybdenum carbide samples, with varying amounts of CO chemisorption uptake (measured by ex situ CO chemisorption, 323 K) achieved by aging or treating the catalysts under different pretreatment conditions (see Table S4 for detailed information on pretreatment conditions), which is consistent with the experimental observation that the net effect of oxygen incorporation, at least above the amount of oxygen required for Mo_2C catalysts to reach steady state anisole HDO rates (i.e., exclusive Ar−O bond cleavage; see section 3.2), is to alter the observed benzene synthesis rates per gram of catalyst but not the benzene synthesis rate per active site.

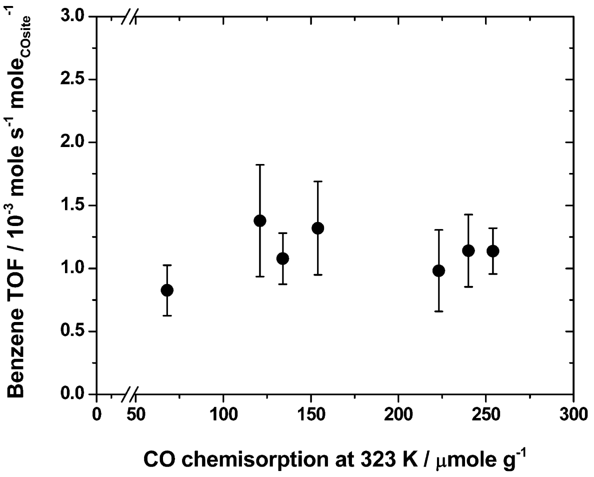

Figure 7. Benzene TOF determined by in situ CO titration for Mo_2C samples with different CO chemisorption uptakes achieved via different sample pretreatment conditions (Table S4). Data shown represent the average of multiple (7−31 times) individual titration experiments with different CO co-fed flow rates and different catalyst loadings, as reported in Tables 1, S2, S3. Error bars represent one standard deviation of multiple titration experiments in the corresponding experiment set.

CO has been generally accepted as a probe molecule to titrate metallic sites through its π-bond donation from the antibonding

Table 5. CO Chemisorption Uptake and Benzene Synthesis Rate of Vapor Phase Anisole HDO for MoO_3 Samples Pretreated in Either Pure H_2 or CH_4/H_2 Mixtures Using Different Temperature Protocols

sample	cat. pretreatment[a]	x for MoO_x	CO chemisorption (μmol g^{-1})	benzene synth rate ($\times 10^{-10}$ mol s^{-1} g^{-1})[c]	benzene synthesis rate ($\times 10^{-5}$ mol s^{-1} $mol_{COsite}{}^{-1}$)[c]
1	H_2, RT (35 min)−675 K (1 h)−423 K	2.8	9.4[b]	2.6	2.8
2	H_2, RT (35 min)−675 K (3 h)−423 K	2.5	33[b]	4.6	1.4
3	H_2, RT (35 min)−673 K (6 h)−423 K	1.7	87.1	23.1	2.7
4	15% CH_4/H_2, 423 K (30 min)−648 K−973 K (150 min) (2 h)−423 K[d]			1110	19−37

[a] See section 2.1 for the nomenclature of the temperature protocols. Catalyst loading was ~0.42 g for all the experiments. [b] An average value of two independent CO chemisorption measurements: 7.9 and 10.8 μmol g^{-1} for $MoO_{2.8}$, and 34.7 and 31.3 μmol g^{-1} for $MoO_{2.5}$. CO chemisorption values reported represent independent experiments performed by loading ~0.42 g of MoO_3 into a chemisorption cell, followed by the corresponding H_2 treatment, as shown in this Table. [c] Data reported as an average value between 1 and 2 h time-on-stream. Figure S11 shows benzene synthesis rates vs time-on-stream for sample no. 3. Reactions were carried out at ~423 K under ambient pressure. Reaction feed composition: anisole/H_2 (vol %) = ~0.15/bal with total flow rate ~1.67 cm^3 s^{-1}. Catalyst mass ~0.42 g was used to calculate benzene synthesis rates. [d] Sample no. 4 was obtained by in situ carburization of sample no. 1 after it was tested for anisole HDO for ~25 ks. Carburization was carried out in a flow of 15% CH_4/H_2 at ~2.11 cm^3 s^{-1} with a designated temperature protocol. After carburization, sample no. 4 was first tested for vapor phase anisole HDO at 423 K at 1 atm for ~30 ks. Sample no. 4 was then recarburized using the same carburization conditions described above, followed by an independent measurement of vapor phase anisole HDO rates for ~11 ks. Data reported as an average value between 1 and 2 h time-on-stream for the two independent anisole HDO measurements. Rates were normalized to ~0.306 g of Mo_2C by considering a stoichiometric conversion from MoO_3 to Mo_2C. CO chemisorption uptake values of ~300−600 μmol g^{-1} were used to normalize benzene synthesis rates per CO chemisorption site shown in this table.

orbital to metals; however, CO can also be used to titrate Lewis acid sites, which can accept the lone pair from CO. The latter case would be similar to an "oxygen vacancy" on the surface of Mo oxycarbide.[28] The potential active sites involved in vapor phase anisole HDO can be, therefore, Mo metallic sites or surface oxygen vacancy sites, although we cannot distinguish between these two scenarios on the basis of the in situ CO titration results.

3.6. Vapor Phase Anisole HDO of MoO_x Catalysts.

Recently, Prasomsri et al.[29] showed that MoO_3 can also selectively cleave the phenolic C−O bond to convert anisole to benzene in the vapor phase with ~39% yield at ~673 K under ambient pressure. In this work, we assess the rate of vapor phase anisole HDO on bulk molybdenum oxide (MoO_x) at lower reaction temperatures (~423 K) and compare oxide and carbide formulations for low temperature HDO. Table 5 shows both CO chemisorption uptake and the corresponding benzene synthesis rate for MoO_x formulations prepared by treating MoO_3 under different H_2 treatment conditions prior to vapor phase anisole HDO at ~423 K under ambient pressure. MoO_3 (identified by XRD, JCPDS 035-0609, Figure S10 in the SI) treated in H_2 at ~675 K for 1, 3, and 6 h was progressively reduced to $MoO_{2.8}$, $MoO_{2.5}$, and $MoO_{1.7}$, respectively, in which the stoichiometry of the reduced formulations was assessed on the basis of quantification of the water removed during the H_2 treatment. The reduction of MoO_3 was further confirmed by XRD analysis in which the diffraction pattern of the spent $MoO_{1.7}$ catalyst was found to match that of MoO_2 (JCPDS 032−0671), as shown in Figure S10. Both the benzene synthesis rate per gram of catalyst and the CO chemisorption uptake were found to increase as the extent of reduction of the MoO_3 catalysts increases (Table 5), presumably because of the increasing number of Lewis acid sites (oxygen vacancies).[22]

A typical plot of benzene synthesis rate per gram of catalyst as a function of time for the $MoO_{1.7}$ catalyst is shown in Figure S11 in which the catalyst was found to suffer from continuous deactivation over the course of the investigation (~20 ks). Benzene and methanol were the only products observed for samples 1−3 in Table 5. Because metallic sites in Mo_2C catalysts assessed by ex situ CO chemisorption were found to correlate with measured rates of vapor phase anisole HDO,[3] the average benzene synthesis rate between 1 and 2 h time-on-stream was normalized to the CO chemisorption uptake, and it was found to be nearly invariant ($2.3 \pm 0.8 \times 10^{-5}$ mol s^{-1} $mol_{COsite}{}^{-1}$), suggesting that metallic sites associated with H_2-treated MoO_3 catalysts are involved in vapor phase anisole HDO (Table 5). Benzene synthesis rates per CO chemisorption site for the MoO_x catalysts ($2.3 \pm 0.8 \times 10^{-5}$ mol s^{-1} $mol_{COsite}{}^{-1}$), however, were found to be at least 10 times lower than that for typical Mo_2C catalysts (~4×10^{-4} mol s^{-1} $mol_{COsite}{}^{-1}$; Table 3).

In situ carburization of the $MoO_{2.8}$ catalyst, after ~25 ks time-on-stream for vapor phase anisole HDO, was carried out prior to kinetic measurements (denoted as sample no. 4 in Table 5) to demonstrate the difference in the benzene synthesis rates over carbidic and MoO_x sites (see Scheme S1 in the SI for the evolution of MoO_3 catalysts under different pretreatment conditions). The benzene synthesis rate per gram of catalyst (average value of two independent measurements) for the "oxygen-exposure-free" carburized sample (sample no. 4 in Table 5) was found to be ~1.1×10^{-7} mol s^{-1} g^{-1}, which is ~50 times higher than that for the $MoO_{2.8}$ catalyst (sample no. 1 in Table 5), and the selectivity of methane (C_1 basis), methanol (C_1 basis), and benzene (C_6^+ basis) were found to be 11, 89, and 97% respectively, which are similar to those obtained using molybdenum carbide catalysts.[3] If we use the CO chemisorption uptake reported by Lee et al.,[5] ~300−600 μmol g^{-1}, to normalize the benzene synthesis rate for this freshly carburized catalyst, the corresponding benzene synthesis rates per CO chemisorption site were ~1.9×10^{-4} to ~3.7×10^{-4} mol s^{-1} $mol_{COsite}{}^{-1}$. These rates are significantly higher (~7−14 times) than those for MoO_x catalysts (Table 5), demonstrating that metallic sites associated with bulk molybdenum oxide catalysts (MoO_x), are much less active for vapor phase anisole HDO at low temperature (~423 K) and ambient pressure as compared with molybdenum carbide catalysts.

4. CONCLUSIONS

Site requirements of molybdenum carbide catalysts for vapor phase anisole HDO were investigated via in situ CO titration, transient kinetic studies, and temperature-programmed surface reaction with H_2. Approximately 1.3 monolayers of oxygen were found to be still retained in a molybdenum carbide catalyst, which was passivated by 1% O_2/He, even after hydrogen treatment at 723 K for 1 h prior to reaction. The further accumulation of ~0.29 monolayer of oxygen (based on BET surface area) during the observed transient in anisole HDO was evidenced from an oxygen mass balance, demonstrating that in situ oxidation of molybdenum carbide by the reactant (anisole) during HDO could not be avoided, even at a high hydrogen-to-anisole molar ratio (~110) in the reactant feed. The TOF for benzene synthesis estimated by in situ CO titration was found to be $1.1 \pm 0.3 \times 10^{-3}$ mol s^{-1} $mol_{COsite}{}^{-1}$ with an assumption that one CO molecule titrates one active site for benzene synthesis, suggesting that <20% of total potential active sites (assessed by ex situ CO chemisorption) are operating during anisole HDO at 423 K under ambient pressure. An oxygen treatment could successfully incorporate oxygen (734 μmol g^{-1}, O/Mo_{bulk} (molar ratio) = 0.075) in molybdenum carbide. The corresponding benzene synthesis rates per gram of catalyst were found to be ~3 times lower in these formulations compared with a freshly prepared molybdenum carbide catalyst. Similar product selectivity, apparent activation energy for benzene formation, and TOF measured by in situ CO titration for the oxygen treated and freshly prepared molybdenum carbide catalysts suggest that the effect of oxygen, at a level of 734 μmol g^{-1}, is to reduce the number of the active sites for anisole HDO. The observed benzene synthesis rates per CO chemisorption site for bulk MoO_x catalysts were found to be ~10 times lower than those for Mo_2C catalysts, suggesting that the dominant active sites for anisole HDO at 423 K under ambient pressure are associated with molybdenum carbide, not bulk molybdenum oxide.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00713.

Estimation of catalyst formulation of passivated Mo_2C catalysts from TPSR, 4 tables of data, 1 scheme, and 11 figures showing results (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Zakzeski, J.; Bruijnincx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M. *Chem. Rev.* **2010**, *110*, 3552−3599.

(2) Rensel, D. J.; Rouvimov, S.; Gin, M. E.; Hicks, J. C. *J. Catal.* **2013**, *305*, 256−263.

(3) Lee, W.-S.; Wang, Z.; Wu, R. J.; Bhan, A. *J. Catal.* **2014**, *319*, 44−53.

(4) Lee, J. S.; Oyama, S. T.; Boudart, M. *J. Catal.* **1987**, *106*, 125−133.

(5) Oyama, S. T. *The Chemistry of Transition Metal Carbides and Nitrides*; Oyama, S. T., Ed.; Springer Science & Business Media: London, New York, 1996; pp 398−413.

(6) Ranhotra, G. S.; Bell, A. T.; Reimer, J. A. *J. Catal.* **1987**, *108*, 40−49.

(7) Schaidle, J. A.; Lausche, A. C.; Thompson, L. T. *J. Catal.* **2010**, *272*, 235−245.

(8) Liu, P.; Rodriguez, J. A. *J. Phys. Chem. B* **2006**, *110*, 19418−19425.

(9) Iglesia, E.; Ribeiro, F. H.; Boudart, M.; Baumgartner, J. E. *Catal. Today* **1992**, *15*, 307−337.

(10) Ribeiro, F. H.; Boudart, M.; Dallabetta, R. A.; Iglesia, E. *J. Catal.* **1991**, *130*, 498−513.

(11) Ribeiro, F. H.; Betta, R. A. D.; Boudart, M.; Baumgartner, J.; Iglesia, E. *J. Catal.* **1991**, *130*, 86−105.

(12) Blekkan, E. A.; Cuong, P.-H.; Ledoux, M. J.; Guille, J. *Ind. Eng. Chem. Res.* **1994**, *33*, 1657−1664.

(13) Choi, J.-S.; Krafft, J.-M.; Krzton, A.; Djega-Mariadassou, G. *Catal. Lett.* **2002**, *81*, 175−180.

(14) Choi, J.-S.; Bugli, G.; Djega-Mariadassou, G. *J. Catal.* **2000**, *193*, 238−247.

(15) Ren, H.; Yu, W.; Salciccioli, M.; Chen, Y.; Huang, Y.; Xiong, K.; Vlachos, D. G.; Chen, J. G. G. *ChemSusChem* **2013**, *6*, 798−801.

(16) Ranhotra, G. S.; Haddix, G. W.; Bell, A. T.; Reimer, J. A. *J. Catal.* **1987**, *108*, 24−39.

(17) Iglesia, E.; Ribeiro, F. H.; Boudart, M.; Baumgartner, J. E. *Catal. Today* **1992**, *15*, 455−458.

(18) Ribeiro, F. H.; Dalla Betta, R. A.; Guskey, G. J.; Boudart, M. *Chem. Mater.* **1991**, *3*, 805−812.

(19) Shannon, S. L.; Goodwin, J. G. *Chem. Rev.* **1995**, *95*, 677−695.

(20) Shou, H.; Davis, R. J. *J. Catal.* **2013**, *306*, 91−99.

(21) DeWilde, J. F.; Chiang, H.; Hickman, D. A.; Ho, C. R.; Bhan, A. *ACS Catal.* **2013**, *3*, 798−807.

(22) Prasomsri, T.; Shetty, M.; Murugappan, K.; Roman-Leshkov, Y. *Energy Environ. Sci.* **2014**, *7*, 2660−2669.

(23) Miyao, T.; Shishikura, I.; Matsuoka, M.; Nagai, M.; Oyama, S. T. *Appl. Catal., A* **1997**, *165*, 419−428.

(24) Leary, K. J.; Michaels, J. N.; Stacy, A. M. *J. Catal.* **1986**, *101*, 301−313.

(25) Sajkowski, D. J.; Oyama, S. T. *Appl. Catal., A* **1996**, *134*, 339−349.

(26) St. Clair, T. P.; Dhandapani, B.; Oyama, S. T. *Catal. Lett.* **1999**, *58*, 169−171.

(27) Lee, W.-S.; Wang, Z.; Zheng, W.; Vlachos, D. G.; Bhan, A. *Catal. Sci. Technol.* **2014**, *4*, 2340−2352.

(28) Delporte, P.; Meunier, F.; Pham-Huu, C.; Vennegues, P.; Ledoux, M. J.; Guille, J. *Catal. Today* **1995**, *23*, 251−267.

(29) Prasomsri, T.; Nimmanwudipong, T.; Roman-Leshkov, Y. *Energy Environ. Sci.* **2013**, *6*, 1732−1738.