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1 **1. Title**

2 Understanding methanol dissociative adsorption and oxidation on amorphous oxide films

3

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18

19 **3. Abstract**

20 Interactions between a transition metal (oxide) catalyst and a support can tailor the number and
21 nature of active sites, for instance in the methanol oxidation reaction. We here use ambient
22 pressure X-ray photoelectron spectroscopy (AP-XPS) to identify and compare the surface

23 adsorbates that form on amorphous metal oxide films that maximize such interactions.
24 Considering $\text{Al}_{(1-x)}\text{M}_x\text{O}_y$ (M=Fe or Mn) films at a range of methanol:oxygen gas ratios and
25 temperatures, we find that the redox-active transition metal site (characterized by methoxy
26 formation) dominates dissociative methanol adsorption, while basic oxygen sites (characterized
27 by carbonate formation) play a lesser role. Product detection, however, indicates complete
28 oxidation to carbon dioxide and water with partial oxidation products (dimethyl ether)
29 comprising a minor species. Comparing the intensity of methoxy and hydroxyl features at a fixed
30 XPS chemical shift suggests methanol deprotonation during adsorption in oxygen rich conditions
31 for high transition metal content. However, increasing methanol partial pressure and lower metal
32 site density may promote oxygen vacancy formation and the dehydroxylation pathway,
33 supported by a nominal reduction in the oxidation state of iron sites. These findings illustrate that
34 AP-XPS and mass spectrometry together are powerful tools in understanding metal-support
35 interactions, quantifying and probing the nature of catalytic active sites, and considering the link
36 between electronic structure of materials and their catalytic activity.

37

38 **4. Introduction**

39 Methanol (CH_3OH) is a versatile and flexible chemical that can be used both as a fuel
40 source and chemical feedstock^{1,2}. CH_3OH oxidation involves a series of oxidation and
41 dehydration reactions³ with numerous potential products depending on the reaction pathway. For
42 example, partial oxidation of CH_3OH can yield formaldehyde (CH_2O), dehydration and C-O
43 coupling produces dimethyl ether ($\text{CH}_3)_2\text{O}$, and complete oxidation yields water (H_2O) and
44 carbon dioxide (CO_2). The methanol oxidation reaction (MOR) can be used as a probe to
45 quantify the density of active sites on oxide surfaces^{4,5}, and due to its diverse potential products

46 and pathways, help ascertain the nature of these active sites⁴. Considering a broad range of metal
47 oxides, CH₂O is formed on redox-active sites, (CH₃)₂O is formed on Brønsted acid sites, and
48 CO₂ is formed on basic sites⁴.

49 The MOR has been studied on transition metals (e.g. V, Cu, Mn, Fe, Mo, Pd, Au) and
50 their oxides with and without supports⁶⁻¹³. Supports not only disperse the catalyst as small
51 particles with high surface area, but also can modify the activity of the catalyst and influence its
52 selectivity towards the different products of MOR. Considering the common support material of
53 γ -alumina, previous reports have shown that this material alone will oxidize CH₃OH to (CH₃)₂O
54 in oxygen rich environments at temperatures <275 °C, above which carbon monoxide (CO)
55 begins to form. By incorporating manganese and iron oxide catalysts onto γ -alumina supports,
56 (CH₃)₂O remained the primary oxidation product but formed at lower temperatures, and above
57 200 °C complete oxidation to CO₂ dominated¹⁴. As oxide supports can carry their own activity
58 towards MOR, the activity of and product distribution from supported catalysts thus depends on
59 the catalyst loading.⁹

60 In order to maximize effects localized to the catalyst-support interface, the interface
61 density can be increased by dispersion of small catalyst nanoparticles. The extension of this is
62 the incorporation of transition metals into a support host directly, thus maximizing electronic
63 interactions and potential dual-active site effects. Herein, we prepare amorphous metal oxides
64 (AMOs) by embedding the transition metal ion into the support, resulting in uniform interaction
65 between “support” and “catalyst” metal centers over the surface of AMOs. Such AMOs find use
66 in many fields ranging from electronics to heterogeneous catalysis¹⁵⁻¹⁷. The electronic structure
67 of these materials can be tailored for a given application, influencing for example their
68 corrosion-resistance properties¹⁸ and electrochemical activity¹⁹.

69 Alumina's acid/base characteristics, which maximize dispersion of transition metal
70 (oxides) on supports, facilitate the incorporation of a wide range of transition metal cations at
71 high concentrations in AMOs¹⁷. The addition of iron (Fe) and manganese (Mn), here model
72 catalyst centers for the MOR, leads to new filled electronic states in alumina-based AMOs at the
73 top of the valence band²⁰. In our previous work, we investigated the influence of these new
74 electronic states on the surface acidity, basicity, and the hydroxylation behavior in a humid
75 environment²¹. In the current work, we study the influence of these new electronic states on the
76 surface reactivity towards CH₃OH.

77 We have used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to
78 investigate CH₃OH oxidation on Al_(1-x)M_xO_y (M = Fe, Mn) AMO films across temperatures and
79 methanol:oxygen gas ratios. For the compositions considered here, Fe and Mn are fully dispersed
80 without evidence of phase segregation and the formation of transition metal oxide clusters¹⁷. The
81 nominal oxidation state of Fe and Mn in the films is +3, and the basicity of the films increases
82 with Fe content. Both methoxy (here referred to as OCH₃) and carbonate (here termed CO₃)
83 species are observed on the surface, where the increase in OCH₃ coverage with increase in
84 transition metal content suggests that transition metal sites are active for CH₃OH oxidation. The
85 Al_(1-x)Fe_xO_y and Al_(1-x)Mn_xO_y oxide films studied here had fewer basic sites (characterized by
86 CO₃ formation) compared to acidic and redox-active sites (characterized by OCH₃ formation).
87 Consideration of OCH₃ and hydroxyl (here termed OH) features in the O 1s and C 1s core levels
88 suggests that the chemical shift for and/or intensity of OH varies with the methanol:oxygen gas
89 ratio and AMO composition.

90

91 **5. Experimental**

92 *Thin-film preparation*

93 Precursor solutions were prepared by mixing different ratios of 1 M aqueous solutions of
94 transition metal nitrate salts, $\text{Mn}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ and 1 M aqueous solution of
95 $\text{Al}(\text{NO}_3)_x(\text{OH})_{3-x}$ clusters, prepared by bulk electrolysis using a procedure from the literature and
96 described previously¹⁷. The solution was spun coat onto a polished Si(100) substrate previously
97 coated with Ti and Ir by electron-beam evaporation to mitigate charging, and annealed at 450°C
98 for 30 min²⁰. The thin films obtained were atomically smooth with a root-mean-square roughness
99 (R_{rms}) <1 nm as determined by atomic force microscopy. The films are referred to by their metal
100 ratios, i.e. a film with 80% Al and 20% Fe is called as Al₈Fe₂.

101 *AP-XPS*

102 AP-XPS was performed at the beamline 9.3.2 at the Advanced Light Source²². Films were placed
103 atop a BN heating element on a sample holder containing no Pt, and grounded through a
104 thermocouple pressed onto the film surface and electrically isolated from the holder with a
105 ceramic. Films were cleaned by UV ozone prior to loading into the sample chamber, and cleaned
106 *in-situ* by heating to 300 °C in an atmosphere of 100 - 150 mTorr of O₂. Following cleaning,
107 films were then cooled to room temperature under 100 mTorr O₂. Films were characterized at
108 room temperature and during a temperature ramp for 10:100, 50:100, and 100:50 mTorr
109 methanol:oxygen gas. Figure S1 shows example survey spectra collected at 690 eV for 50 mTorr
110 CH₃OH and 100 mTorr oxygen at 25 °C for the Al₈Fe₂ and Al₄Fe₆ films depicting the expected
111 features. The incident photon energy was calibrated at room temperature by cross-referencing O
112 1s (690 eV, 750 eV) and Al 2p (490 eV, 350 eV) core levels in duplicate films previously
113 calibrated to the Au 4f (84 eV) of an auxiliary reference²¹, where the resultant O 1s and Al 2p
114 binding energy (BE) is dependent on composition as discussed in section 6.2. Subsequent

115 measurements at elevated temperatures were calibrated to the Al 2p core level as an internal
116 standard. The spectra were fit with CasaXPS using a Shirley-type background subtraction. The
117 identified features were fit using a line shape with 70% Gaussian and 30% Lorentzian character
118 with average fitted values shown in Table S1 and S2. The OH+OCH₃ feature in the O 1s core
119 level was constrained at 1.65 eV above the bulk O 1s BE based on previous measurements made
120 for duplicate films in water²¹, unless stated otherwise.

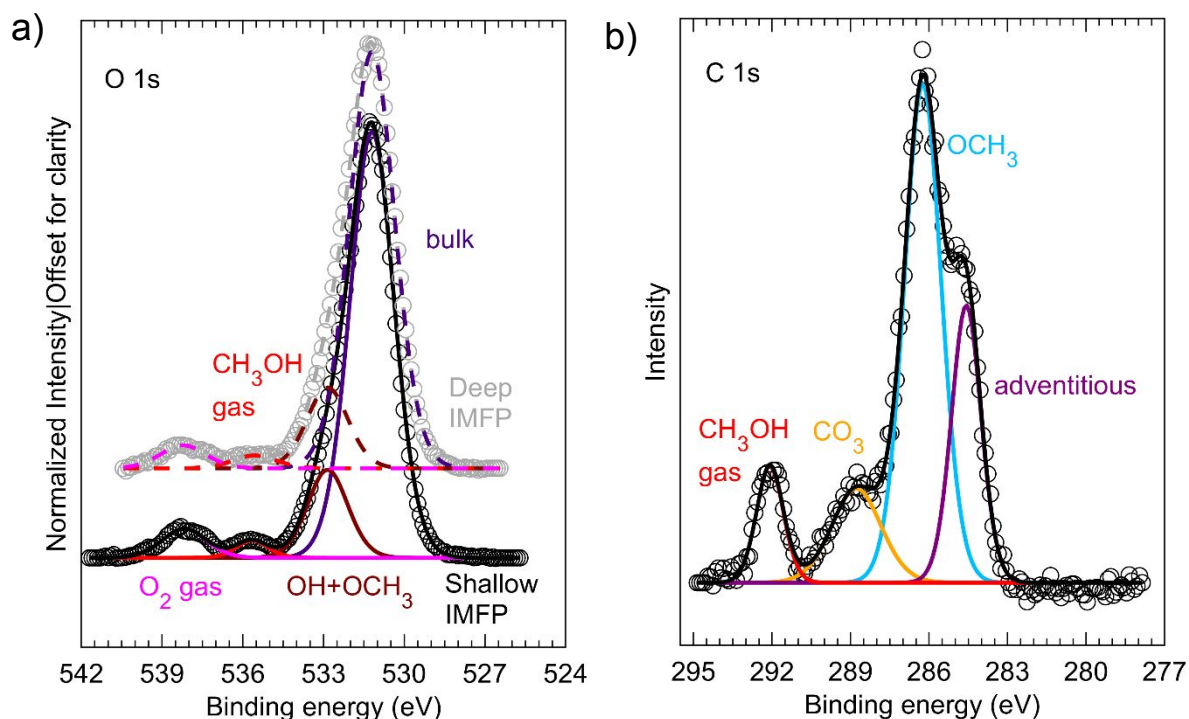
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122 6. Results and Discussion

123 6.1 Feature Identification

124 We first describe the features observed in each core level, considering the example case of 50
125 mTorr CH₃OH and 100 mTorr oxygen at room temperature.

126



127 Figure 1: (a) O 1s and (b) C 1s for Al₈Fe₂ in 50 mTorr of CH₃OH and 100 mTorr of oxygen at
128 a) a) O 1s probed at an incident photon energy (IPE) of 690 eV (shallow inelastic mean free
129 path (IMFP) $\sim 5.8 \text{ \AA}^{23}$, solid line) and 750 eV (deep IMFP $\sim 6.6 \text{ \AA}^{23}$, dashed line). Features at the
130 surface (OH+OCH₃) are less intense when probed with a greater IPE. b) C 1s core level (490 eV
131 IPE) depicting the different features observed.

132

133 **O 1s core level:** For the oxygen core level, four distinct features, shown in Figure 1a), were
134 observed across all samples and conditions. Depth profiling established that the feature at ~ 531
135 eV is due to the bulk of the film, while the higher BE shoulder is due to adsorbates, with
136 integrated intensity ratio of shoulder/bulk as 0.19 and 0.18 in Figure 1 probed at 690 eV (shallow
137 inelastic mean free path (IMFP) $\sim 5.8 \text{ \AA}^{23}$) and 750 eV (deep IMFP $\sim 6.6 \text{ \AA}^{23}$) incident photon
138 energy (IPE). This shoulder at 1.65 eV above the bulk is attributed in part to OH species based
139 on previous measurements of duplicate samples in water²¹. Any oxidized carbon species on the
140 surface will also have similar O 1s BEs, and are primarily attributed to OCH₃ species based on
141 the C 1s spectra (Figure 1b). The relative sensitivity factor (RSF) for O 1s (690 eV) to the C 1s
142 (490 eV) was determined to be 1.08 by measuring gaseous CO₂. The features at $\sim 535 \text{ eV}^6$ and
143 $\sim 538 \text{ eV}^6$ are attributed to gas phase CH₃OH and oxygen, respectively, with their relative
144 intensities consistent with gas-phase partial pressures and experimentally measured O:C RSF.
145 Table S1 shows the average BEs and the full width half maximum (FWHM) of the features
146 observed in the oxygen core level for the films across different methanol:oxygen gas ratios at
147 different temperatures. Example room temperature oxygen core level spectra in Figure S2 depict
148 the changes in feature BE and intensity with film composition and gas ratio.

149 **C 1s core level:** For the carbon core level, four distinct features at $\sim 284.8 \text{ eV}$, $\sim 286.1 \text{ eV}$, \sim

150 288.6 eV and ~ 292 eV were observed as shown in Figure 1 b). The feature at ~ 284.8 eV is
151 adventitious carbon (CH_x)²⁴. The feature at 286.1 eV is at BE consistent with C-O or $\text{C}\equiv\text{O}$ bonds,
152 potentially from a OCH_3 species or CO ²⁵. Although both can be intermediates in MOR, we
153 assign this feature to OCH_3 as it is the predominant intermediate for the MOR on transition
154 metals^{4, 7, 26}. The feature at 288.6 eV arises from CO_3 ²⁷ and the feature at 292 eV from gas phase
155 CH_3OH . A small amount of K was observed on the Al_4Fe_6 sample (Figure S3); based on
156 tabulated cross sections, the abundance of K is $\sim 10\times$ lower than its 2p intensity ratio with C 1s at
157 490 eV. Table S2 shows the average BE and FWHM of the features observed in the carbon core
158 level for the films across different methanol:oxygen gas ratios at different temperatures. Example
159 room temperature carbon core level spectra in Figure S2 depict the changes in feature BE and
160 intensity with film composition and gas ratio.

161 **Metal core levels:** For Al_8Fe_2 , four distinct features at ~ 74 eV, ~ 62 eV, ~ 66 eV and ~ 56 eV
162 were observed as shown in Figure S4. The feature at ~ 74 eV is assigned to the Al 2p core level
163 and that at ~ 56 eV to the Fe 3p core level, whose BE is referred to here as that from a single
164 Gaussian-Lorentzian feature. The features at ~ 62 eV and ~ 66 eV are assigned to the Ir 4f doublet
165 from the conductive substrate coating. Comparing across IPEs with varied mean free paths, the Ir
166 layer remains buried under the $\text{Al}_{(1-x)}\text{M}_x\text{O}_y$ film (Figure S5). A similar spectrum was obtained for
167 the Al_4Fe_6 film as well. For the sample with Mn content, a feature at ~ 47 eV was observed
168 (Figure S4) instead of ~ 56 eV, which is assigned to the Mn 3p.

169

170 **6.2 Electronic structure of the amorphous oxide films**

171 We first consider the electronic structure of the Al_8Fe_2 , Al_4Fe_6 , and Al_6Mn_4 films by
172 comparing their metal and oxygen core levels, as well as the valence band (VB). In all films,

173 fitting of the Fe 3p and Mn 3p (Figure S6-7) core levels gives a nominal oxidation state of +3²⁰.
 174 The oxidation state of the Fe 3p can be assessed using its FWHM (Figure S7) and BE (discussed
 175 in detail in section 6.3.4). While the oxidation state of Fe 3p is predominantly +3 for the different
 176 gas compositions and temperatures, small changes in oxidation state with gas composition and in
 177 some cases temperature (consistent with VB spectra as shown in Figure S8) for Fe-containing
 178 films are discussed in more detail in section 6.3.4. The VB edge, fit with a step down function
 179 and noted at half height, is highest in BE—furthest from the Fermi level—for Al₈Fe₂ (Table 1
 180 and Figure S9), but shifts approximately ~1 eV lower with increasing Fe content in Al₄Fe₆, and
 181 is similar for Al₆Mn₄. For other methanol:oxygen gas ratios, the VB edge is similar for Al₈Fe₂
 182 and Al₆Mn₄, but decreases with increase in Fe content in Al₄Fe₆ (Figure S9). The use of a
 183 conductive Ir underlayer beneath the 5 nm AMO film, grounding of the AMO film surface
 184 through the thermocouple, and presence of gas phase photoelectrons mitigate potential charging
 185 effects. For example, the as measured BE of the bulk O 1s (750 and 690 eV IPE) and Al 2p (690,
 186 490, and 350 eV IPE) of Al₈Fe₂ in 10:100 mTorr methanol:oxygen decreased only ~0.2 eV
 187 upon heating from room temperature to 275 °C, suggesting minimal potential charging effects.

Core level	BE for Al ₈ Fe ₂ (eV)	BE for Al ₄ Fe ₆ (eV)	BE for Al ₆ Mn ₄ (eV)
O 1s (bulk)	531.4	530.9	531.2
Al 2p	74.2	74	74.3
M 3p	56.1	55.7	48.8
VB edge	3.7	2.7	2.5

188 Table 1: BE of the bulk O 1s, Al 2p, M 3p and VB edge for Al₈Fe₂, Al₄Fe₆ and Al₆Mn₄ films
 189 for 50 mTorr of CH₃OH and 100 mTorr of oxygen at 25 °C.

190 Similarly, both the bulk O 1s feature and the Fe 3p shift to ~ 0.5 eV and ~ 0.4 eV lower
191 BE with increasing Fe content (Figure S9). This could include effects from a shift in the rigid
192 electronic structure (lesser charging) with Fe substitution, given the shift of VB edge towards the
193 Fermi level, however we note that at the same IPE, the VB edge shifts by 1 eV while the Al 2p
194 shifts by only 0.2 eV. Thus, a lower bulk O 1s BE may also indicate a greater basicity (electron
195 density) on O, though surprising given the more covalent nature of Fe-O versus Al-O bonds
196 based on electronegativity differences. In addition, the bulk O 1s feature shifts to lower BE for
197 more reducing methanol:oxygen gas ratios with increasing temperature (Figure S10).

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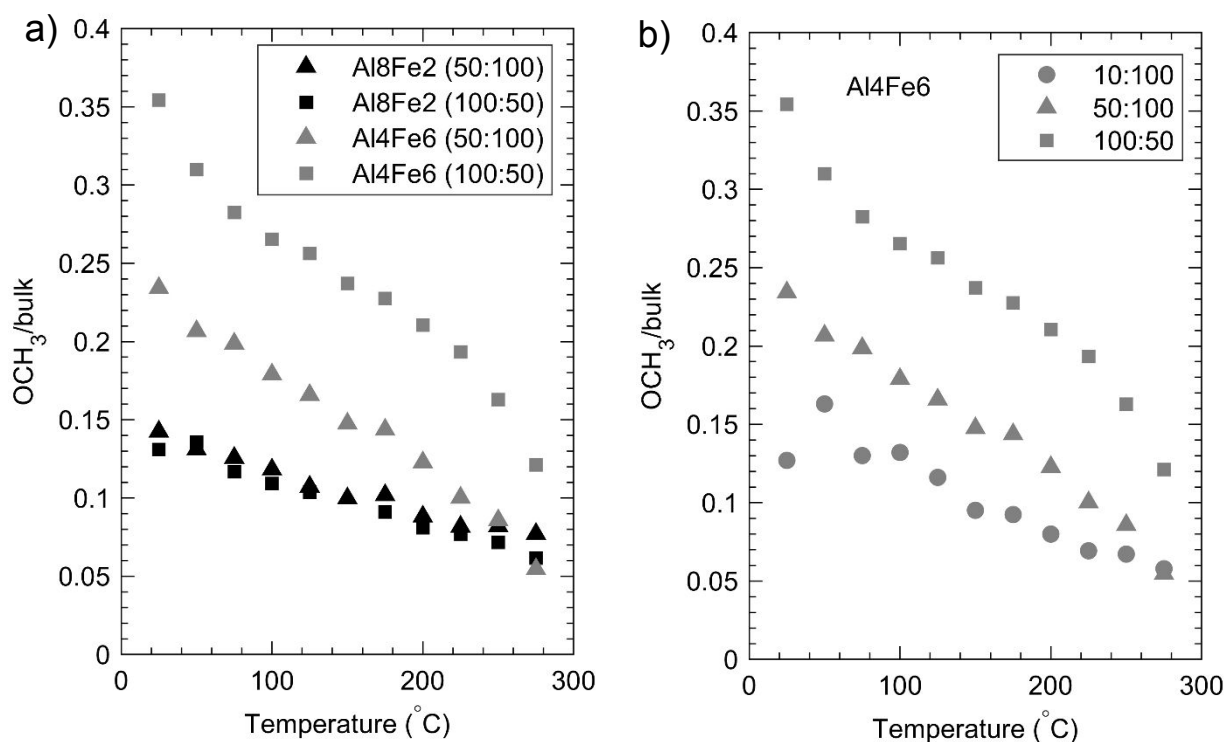
199 **6.3 Adsorbate formation and mechanistic implications**

200 We next consider the surface speciation and its relation to AMO composition and
201 electronic structure. On oxides, CH₃OH dissociatively adsorbs to form CH₃O groups either by
202 deprotonation at a metal site or dehydroxylation at an oxygen site. The metal site (*M*) is
203 considered redox-active ($O + M + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}-M + \text{H}-O$), whereas a surface *O*-H group
204 can give up a proton (acidic character) to dehydrate CH₃OH in this process ($\text{H}-O + \text{CH}_3\text{OH} \rightarrow$
205 $\text{CH}_3-\text{O} + \text{H}_2\text{O}$)⁴. OCH₃ groups can subsequently deprotonate to form CH₂O, or C-O coupling can
206 occur between a CH₃ group and CH₃O-*M* to form (CH₃)₂O. Adsorbed CO₃ is expected to form at
207 basic sites as a precursor to CO₂ desorption ($\text{O}_2\text{C}-O \rightarrow O + \text{CO}_2$). We consider the relative
208 abundance of OCH₃ and CO₃ surface species as obtained by the fitting of the C 1s spectra for
209 different methanol:oxygen gas ratios (noted in mTorr) and temperature to understand the nature
210 of AMO active sites for MOR.

211

212 **6.3.1 Formation of adsorbates across compositions and conditions**

213 Changes in film composition can affect the formation of OCH₃ groups. The intensity of
214 the OCH₃ (C 1s) normalized to that of the bulk oxide (O 1s) is compared across Fe-containing
215 samples (Figure 2). If the intensity of bulk O is not attenuated appreciably by other species, such
216 as adventitious carbon, this ratio is proportional to elemental coverage²⁸. As expected with an
217 increase in thermal energy, the OCH₃/bulk ratio decreases with increase in temperature. We note,
218 however that the steeper decrease for Al₄Fe₆ for temperatures > 150 °C is commensurate with
219 observed conversion to CO₂ and H₂O (Figure S11). The OCH₃ coverage is greater for Al₄Fe₆
220 compared to Al₈Fe₂ for all methanol:oxygen gas ratios, indicating that Fe is active for OCH₃
221 formation. While the OCH₃/bulk ratio at room temperature increases with the partial pressure of
222 CH₃OH in the chamber, indicating sub-monolayer concentration on the surface, this increase is
223 smallest on Al₈Fe₂ (and negligible comparing 50:100 and 100:50 methanol:oxygen gas ratios),
224 further confirming the role of Fe in OCH₃ formation. The drop in OCH₃/bulk ratio with
225 increasing temperature is larger for Al₄Fe₆ (77% for 50:100 methanol:oxygen gas ratio) than
226 Al₈Fe₂ (46%) which may indicate that while substitution of more acidic Fe for Al increases the
227 number of sites for OCH₃ formation, it also reduces the strength of their binding or facilitates
228 their oxidative removal.



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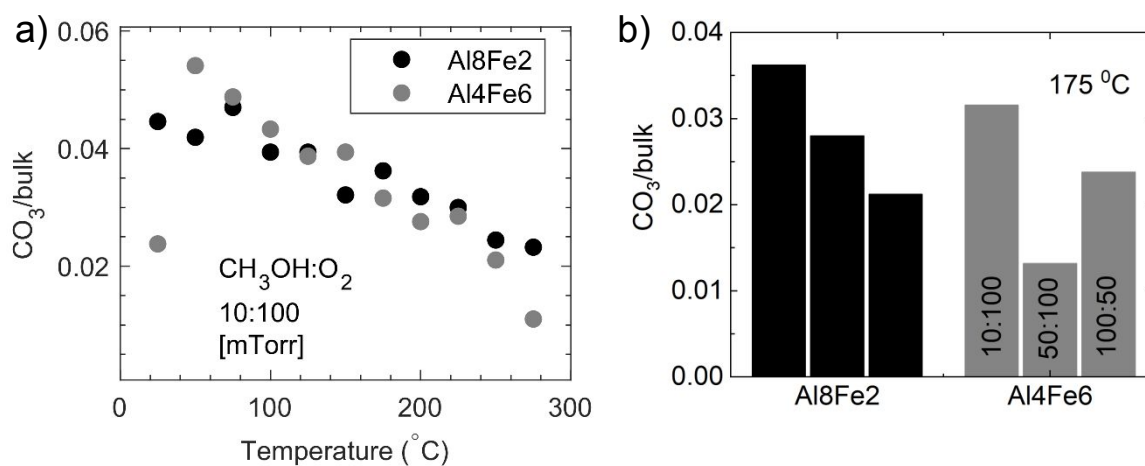
230 Figure 2: Ratio of OCH_3 (C1s) to the bulk (O1s) with temperature for a) Al_8Fe_2 and Al_4Fe_6 for
 231 50:100 and 100:50 methanol:oxygen gas ratios and b) Al_4Fe_6 for different gas ratios, where the
 232 OCH_3 coverage increases with CH_3OH partial pressure in the reactant gas. In the above figure,
 233 10:100, 50:100 and 100:50 denote the pressures of methanol:oxygen in mTorr.

234

235 To assess the coverage of CO_3 (expected at basic sites as a precursor to CO_2 desorption),
 236 its intensity is calculated relative to the bulk. The CO_3/bulk ratio is comparable on both Fe-
 237 containing films (Figure 3 and Figure S12). The shift in bulk O 1s to lower BE from Al_8Fe_2 to
 238 Al_4Fe_6 is consistent with an increase in basicity of the O^{2-} sites upon incorporation of Fe^{3+} into
 239 the Al^{3+} -oxide host (Table 1, Figure S9). The comparable CO_3/bulk ratio for these two films may
 240 thus suggest basic sites are not the primary contributor to CH_3OH oxidation under these

241 conditions, assessed more in the following section. The CO_3/bulk ratio decreases with
 242 temperature for all film compositions (Figure S12). Generally, the amount of CO_3 on the surface
 243 also decreases with decreasing partial pressure of oxygen as shown in Figure 3, as would be
 244 expected given its production from complete CH_3OH oxidation at a stoichiometric 3:2
 245 methanol:oxygen ratio. A notable exception is Al_4Fe_6 in 100:50 mTorr methanol:oxygen, which
 246 has greater CO_3 coverage compared to 50:100 mTorr methanol:oxygen.

247



248

249 Figure 3: Ratio of the CO_3 (C1s) to bulk (O1s) for a) Al_8Fe_2 and Al_4Fe_6 for 10 mTorr of
 250 CH_3OH and 100 mTorr of oxygen with temperature and b) Al_8Fe_2 and Al_4Fe_6 at $175\text{ }^\circ\text{C}$ for
 251 noted methanol:oxygen gas pressures [mTorr].

252

253 6.3.2 Nature of active site

254 To better understand the nature of the active site and pathway for CH_3OH oxidation, we
 255 consider the relative coverage of CO_3 and OCH_3 species (Figure 4). The CO_3/OCH_3 ratio is
 256 similar (0.3-0.4) across films in 10:100 mTorr of methanol:oxygen.

257 The CO_3/OCH_3 ratio tells the ratio of the number of basic (CO_3 forming) to acidic and
258 redox-active (OCH_3 forming) sites. For all films considered here, the number of basic sites is
259 more than two times lower than the total number of acidic and redox-active sites. The CO_3/OCH_3
260 ratio decreases with increase in CH_3OH partial pressure indicating that the formation of CO_3
261 (completely oxidized product) decreases as oxygen partial pressure is decreased, also evident
262 from considering the $\text{CO}_3/\text{bulk oxide}$ ratio (Figure 3, S12). For amorphous Al_4Fe_6 , we observe
263 complete oxidation products of CO_2 and H_2O with a mass spectrometer for both 10:100 and
264 50:100 methanol:oxygen ratios (Figure S10) starting at 150 °C, but not $(\text{CH}_3)_2\text{O}$ at any
265 temperatures. For amorphous Al_6Mn_4 in 50:100 methanol:oxygen, CO_2 and H_2O are produced
266 starting at 200 °C, with small amounts of $(\text{CH}_3)_2\text{O}$ at lower temperatures (Figure S11), although
267 we note that the quantification of evolved gases in the spectrometer is not calibrated. More
268 notable complete oxidation products on Al_4Fe_6 , compared to Al_6Mn_4 , is consistent with both
269 the lower CO_3/OCH_3 ratio (Figure 4) and the concurrent greater reduction in adsorbed OCH_3 as
270 temperature is increased (Figure 2).

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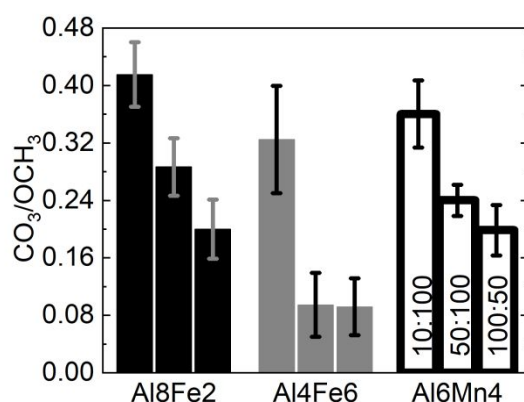
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279 Figure 4: Average ratio of CO₃ (C 1s) to OCH₃ (C1s) species taken across temperatures for the
280 Al₈Fe₂, Al₄Fe₆ and Al₆Mn₄ films. The relative abundance of CO₃ decreases with increasing the
281 CH₃OH partial pressure in the reactant gas. In the above figure, 10:100, 50:100 and 100:50
282 denote the pressure of methanol:oxygen in mTorr.

283

284 **6.3.3 Mode of methanol dissociation on the films**

285 We next examine the intensity ratio of the OCH₃ and OH features to ascertain the mode
286 of CH₃OH activation on the surface. In the O 1s, these features cannot be distinguished and are
287 fit as a single peak. In the C 1s, a distinct OCH₃ feature is fit. As the experimentally measured
288 RSF of O:C is close to 1, taking the ratio of the OH+OCH₃ feature in the O 1s (fit at a chemical
289 shift of 1.65 eV from the bulk) to the OCH₃ feature in the C 1s (approximately 1.6 eV relative to
290 adventitious carbon), here referred to as the O:C ratio (Figure 5), readily approximates the
291 abundance ratio of these adsorbates, provided they are observable at the fit chemical shift. We
292 note that the lower abundance of CO₃ on the surface, which is similar across samples and
293 conditions, is not fit in the O 1s and would result in a roughly consistent offset to this ratio.
294 CH₃OH has been previously proposed⁵ to adsorb dissociatively by forming surface OCH₃ groups
295 with the oxygen atom bonding to the metal site (CH₃O-*M*) and the proton from the alcoholic
296 group bonding to a nearby lattice oxygen site forming *O*-H on the surface. An O:C ratio greater
297 than 1 is consistent with both OCH₃ and OH groups giving rise to distinct XPS chemical shifts in
298 the O 1s. The reduction in O:C ratio with increasing CH₃OH partial pressure for Al₄Fe₆ suggests
299 some O species may not give rise to distinct chemical shifts (or a smaller shift poorly fit in the
300 fixed binding energy offset employed here), or the removal of OH groups (probably as H₂O)
301 from the surface, with lattice oxygen replenished by O₂ gas. The value of the fit O:C ratio is

302 greater when the BE of the O 1s OH+OCH₃ feature floats freely, however the ratio for Al₄Fe₆
303 remains higher than that for Al₈Fe₂ at low CH₃OH partial pressure and comparable under
304 reducing conditions (Figure S13). Al₈Fe₂ maintains comparable O:C ratio with CH₃OH partial
305 pressure, however the Al₆Mn₄ O:C ratio decreases with increase in methanol partial pressure,
306 just as for Al₄Fe₆, with relaxed fit.

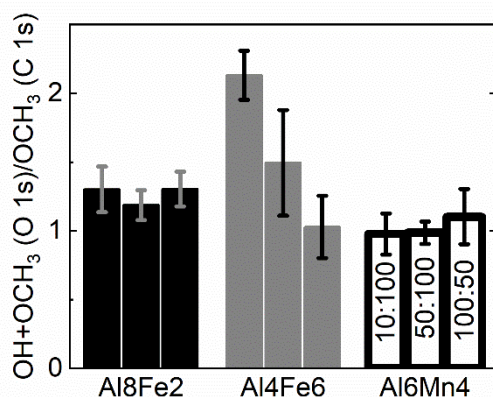
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313 Figure 5: Average across temperatures for the ratio of OH+OCH₃ feature (O 1s) to OCH₃ feature

314 (C 1s) for different methanol:oxygen gas pressures for the Al₈Fe₂, Al₄Fe₆ and Al₆Mn₄ films.

315 In the above figure, 10:100, 50:100 and 100:50 denote the pressure of methanol:oxygen in

316 mTorr.

317 The higher O:C ratio for Al₄Fe₆ at low CH₃OH pressures may indicate that the increased

318 basicity of O sites upon Fe incorporation result in robust O 1s XPS chemical shifts at low OCH₃

319 coverage but less so as Fe sites become saturated. This is consistent with Al₈Fe₂, with constant

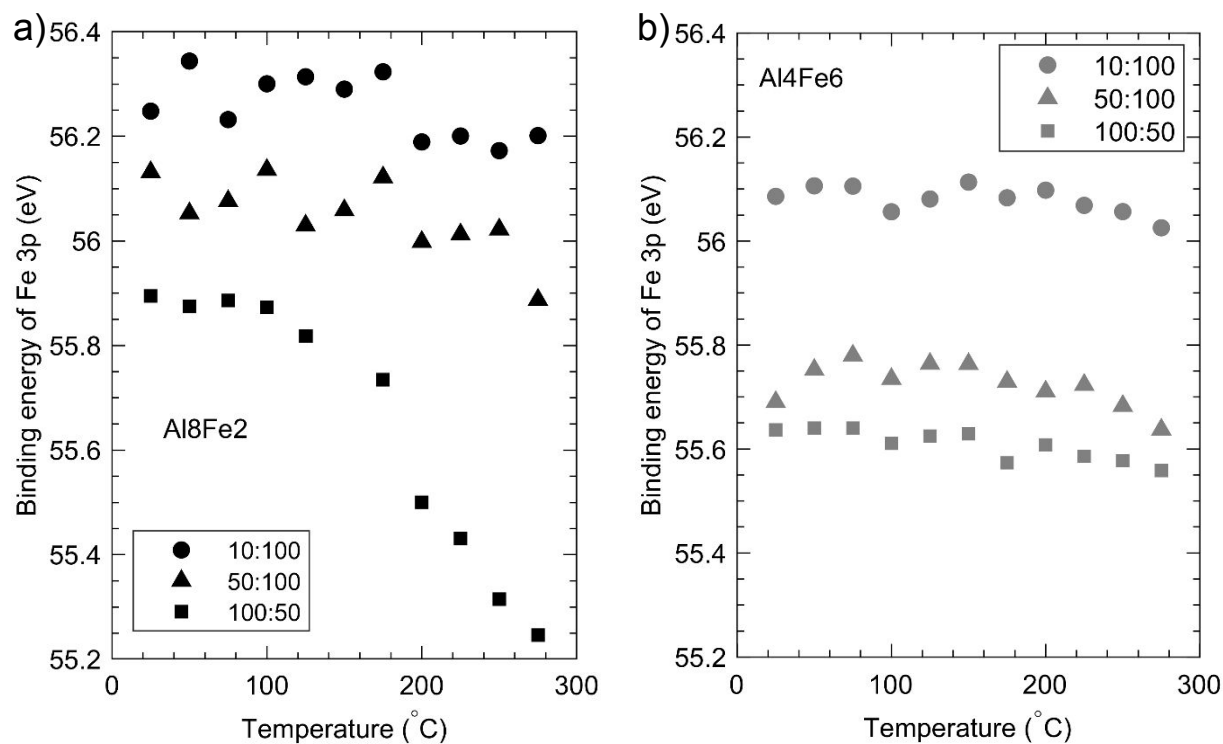
320 OCH₃ coverage indicating site saturation, having a low O:C ratio regardless of CH₃OH partial

321 pressure.

322

323 **6.3.4 Changes in Fe electronic structure**

324 To further assess the role of transition metal in activating CH₃OH, we consider potential
325 changes in Fe valence. The BE of Fe 3p remains similar with temperature but decreases with
326 increase in CH₃OH partial pressure in the reactant gas (Figure 6 and Figure S9). Considering the
327 negligible change in OCH₃ coverage with increase in partial pressure of CH₃OH for Al₈Fe₂,
328 suggesting saturation of active sites, this decrease may result from the formation of oxygen
329 vacancies under more reducing conditions. Oxygen vacancies may similarly contribute to the
330 observed Fe 3p shift to lower BE in Al₄Fe₆, however the increase in OCH₃ coverage on Al₄Fe₆
331 with CH₃OH pressure might also result in Fe reduction. In contrast to other conditions, the Fe 3p
332 BE of Al₈Fe₂ in a 100:50 methanol:oxygen gas ratio decreases with increasing temperature,
333 commensurate with a new feature below the VB edge consistent with the presence of Fe²⁺
334 (Figure S8). Observable reduction of Fe in Al₈Fe₂, but not Al₄Fe₆, might arise from a larger
335 proportion of the Fe sites (presumed saturated with OCH₃ species on Al₈Fe₂) driving CH₃OH
336 (partial) oxidation with increasing temperature.



337
 338 Figure 6: BE of Fe 3p with temperature for a) Al₈Fe₂ and b) Al₄Fe₆ for different
 339 methanol:oxygen gas ratios. In the above figure, 10:100, 50:100 and 100:50 denote the pressure
 340 of methanol:oxygen in mTorr.

341

342 7. Discussion

343 In this study, we have incorporated transition metals (Fe, Mn) into an amorphous Al
 344 oxide host as a model of highly dispersed catalyst/support for the MOR. Cations with d⁵ (Fe³⁺)
 345 and d⁴ (Mn³⁺) electronic configuration add new electronic states at top of the VB edge and within
 346 the bandgap of alumina^{17, 20}. Further, the average coordination number of the Fe³⁺ and Mn³⁺ in
 347 the films considered is similar to that of alumina, ~4.5, indicating dispersed substitution for Al
 348 within the amorphous host without phase segregation. In these films, the interaction between
 349 “catalyst” (Fe, Mn ions) and “support” (Al oxide) is extended uniformly across the surface, as

350 evidenced by the shift in VB maximum and bulk oxygen BE towards the Fermi level with Fe
351 content (Figure S7). However, this increase in oxygen basicity did not translate to increased
352 coverage of CO_3 on the surface under MOR conditions, suggesting that oxygen sites do not
353 dominate CH_3OH activation. With low metal content, the coverage of OCH_3 was independent of
354 CH_3OH partial pressure, suggesting saturation of active sites. In contrast, OCH_3 coverage
355 increased with CH_3OH partial pressure at higher metal content, consistent with CH_3OH
356 activation primarily occurring at these redox-active sites whose oxidation state lowered with
357 OCH_3 adsorption.

358 Previous reports have incorporated manganese and iron oxide catalysts onto γ -alumina
359 supports, which lowered the temperature of MOR compared to the support alone in an
360 approximately 10:100 methanol:oxygen ratio¹⁴. At low temperatures, $(\text{CH}_3)_2\text{O}$ was the primary
361 oxidation product, while complete oxidation to CO_2 dominated above 200 °C. For AMO films,
362 despite the greater coverage of OCH_3 compared to CO_3 species, little to no $(\text{CH}_3)_2\text{O}$ is observed
363 on Al_4Fe_6 , with small amounts forming at temperatures as low as ~50 °C on Al_6Mn_4 .
364 Formation of $(\text{CH}_3)_2\text{O}$ requires C-O coupling between two adjacent $(\text{O})\text{CH}_3$ groups, which may
365 be limited by the dispersion of active transition metal sites in the solid-substitution amorphous
366 films considered here. In contrast, complete oxidation to CO_2 and H_2O is observed at 150 °C—
367 lower in AMOs than discrete supported catalysts by 50 °C—indicating that dispersing metal sites
368 in amorphous oxide hosts is a promising route to maximize support effects in MOR.

369

370 **8. Conclusions**

371 We have employed AP-XPS to study the role of transition metal and its concentration on
372 the dissociative adsorption and oxidation of methanol on amorphous $Al_xM_{(1-x)}O_y$ films, where
373 $M=Fe$ or Mn . Alumina's acid/base characteristics, which maximize dispersion of transition metal
374 (oxides) on supports, facilitate their incorporation at high concentrations in AMOs. We here find
375 that this dispersion in an amorphous framework reduces the temperature of complete methanol
376 oxidation compared to supported MO_x/Al_2O_3 systems in literature and promotes complete
377 oxidation over C-O coupling. The transition metal site (Fe, Mn) was redox-active, leading to the
378 formation of OCH_3 groups whose coverage increases with transition metal content, indicating
379 that the transition metal sites are active for the MOR. By comparison, the basic O^{2-} sites formed
380 adsorbed CO_3 species with roughly comparable coverages across samples and conditions, present
381 at roughly half the concentration of OCH_3 groups. Oxygen vacancy formation is supported by
382 slight reductions in Fe valence (though remaining primarily +3) with increase in methanol partial
383 pressure for the AMO films. These findings illustrate the nature of active sites for the MOR on
384 AMO films and suggest dispersion of transition metals within an amorphous matrix offers new
385 handles to tailor activity and selectivity in oxidation reactions.

386

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