

## Supplementary Materials

# High-temperature abatement of N<sub>2</sub>O over FeO<sub>x</sub>/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts: the effects of oxygen mobility

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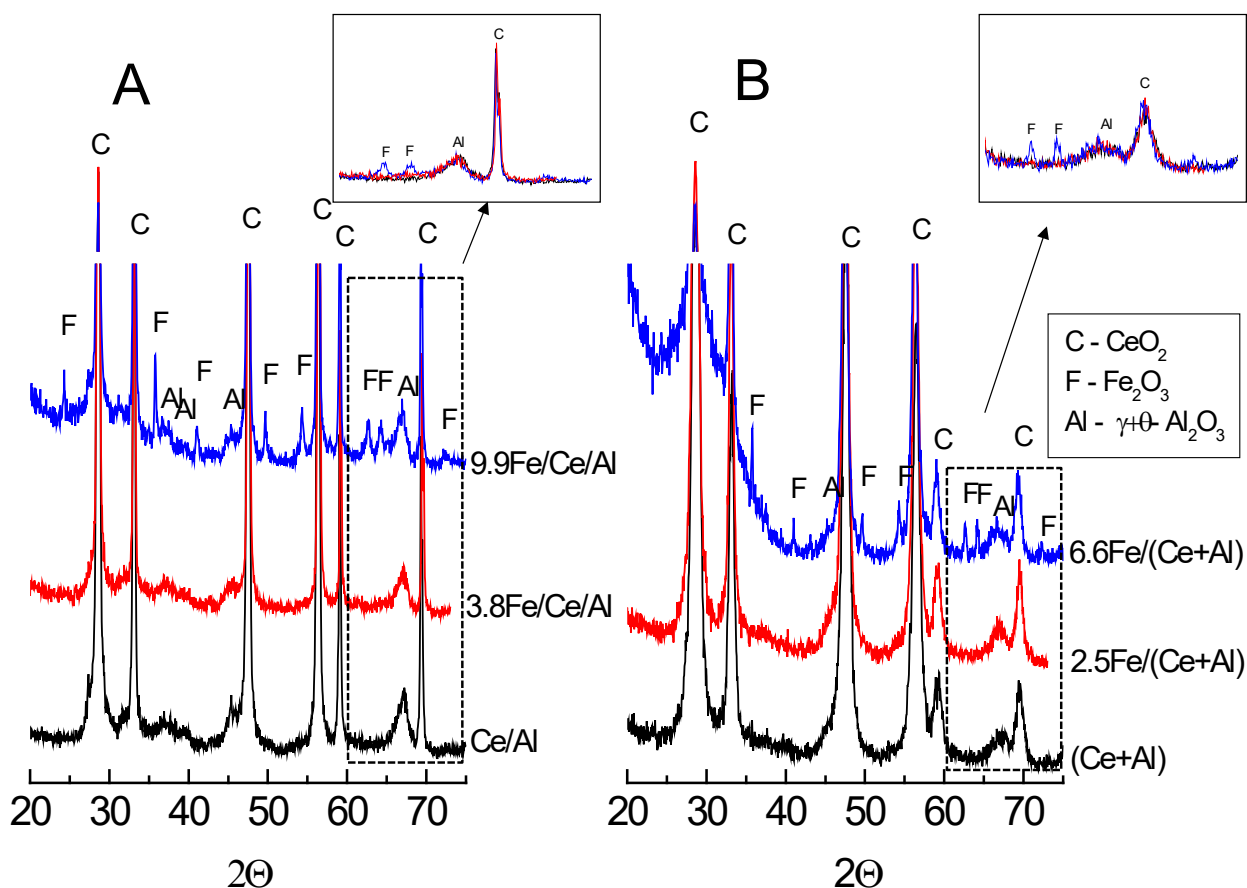
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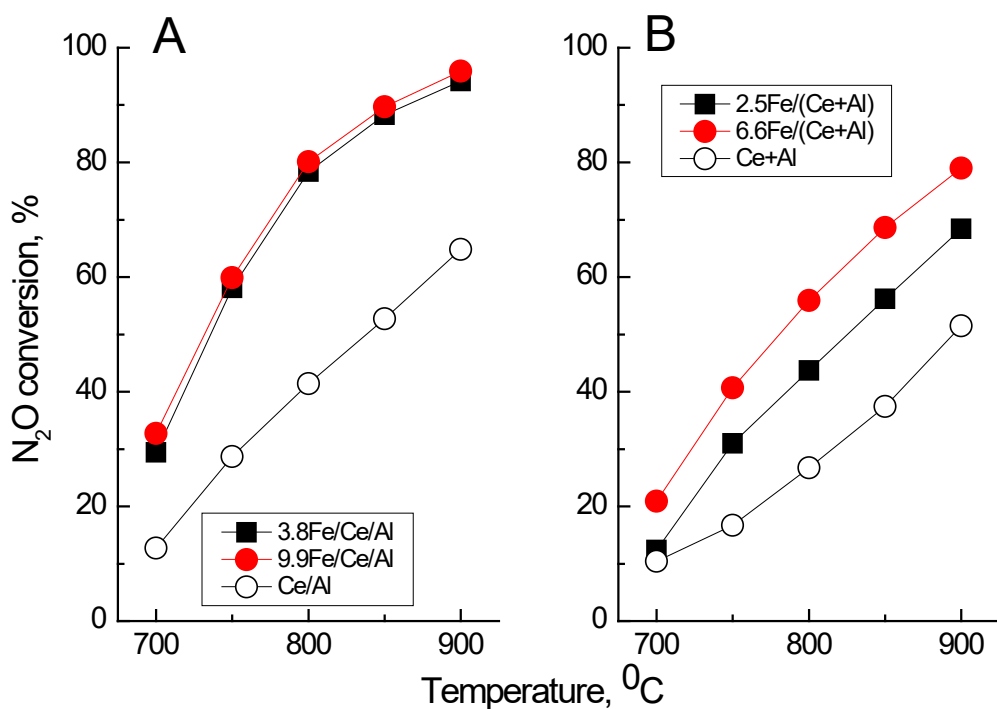
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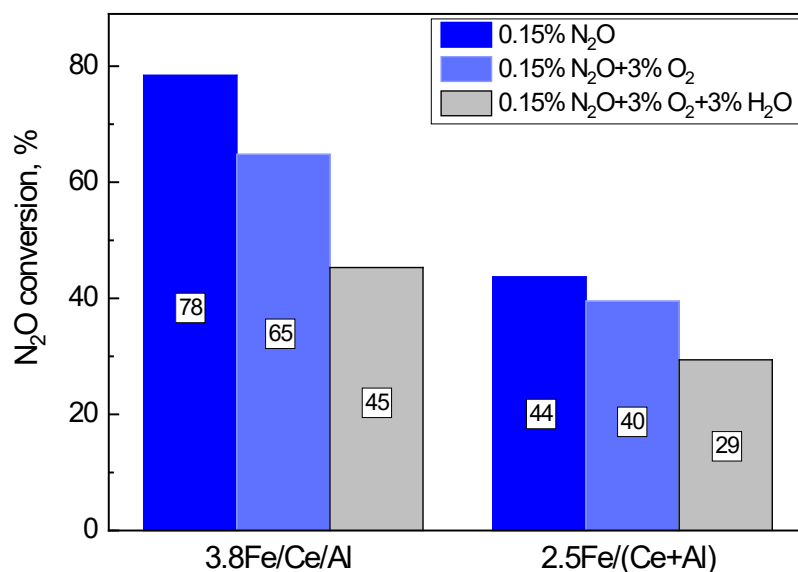
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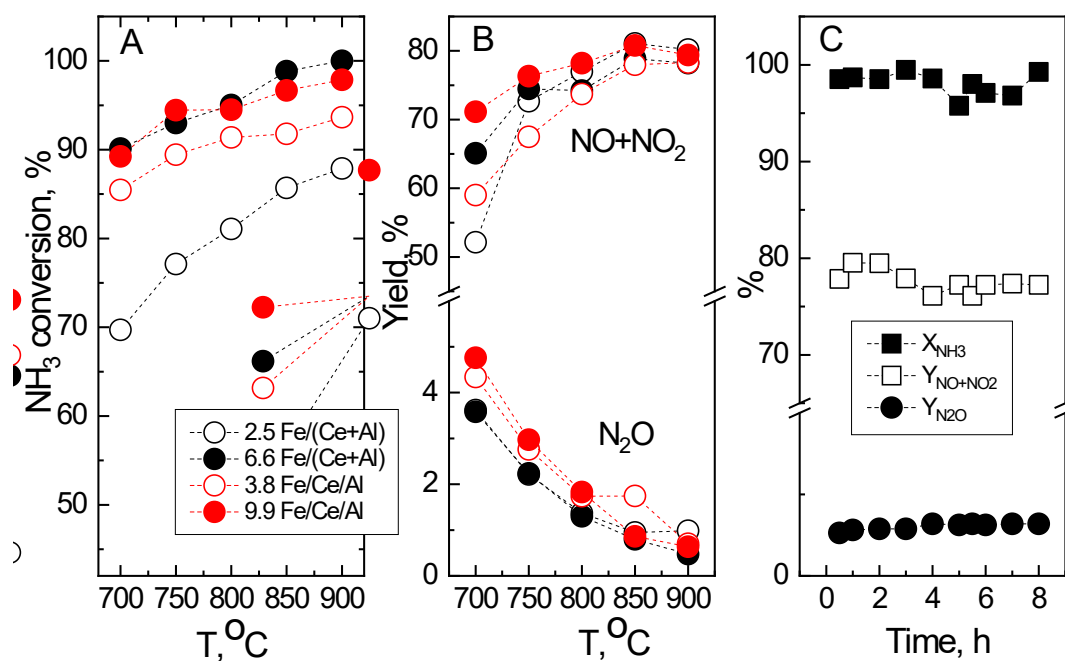
**Figure S1.** XRD patterns of Ce/Al (A) and (Ce+Al) (B) based samples with different content of Fe.



**Figure S2.** Dependence of  $\text{N}_2\text{O}$  conversion on the temperature for Ce/Al (A) and (Ce+Al) (B) based samples.



**Figure S3.** Effect of O<sub>2</sub> and H<sub>2</sub>O presence in the inlet flow on N<sub>2</sub>O conversion over 3.8Fe/Ce/Al and 2.5Fe/(Ce+Al) samples. T = 800°C



**Figure S4.** Temperature dependence of the conversion (A) yield of (NO+NO<sub>2</sub>) and N<sub>2</sub>O (B) at NH<sub>3</sub> oxidation over different Fe/Ce-Al-O based samples. Stability tests for 9.9Fe/Ce/Al sample (C) at 800°C.

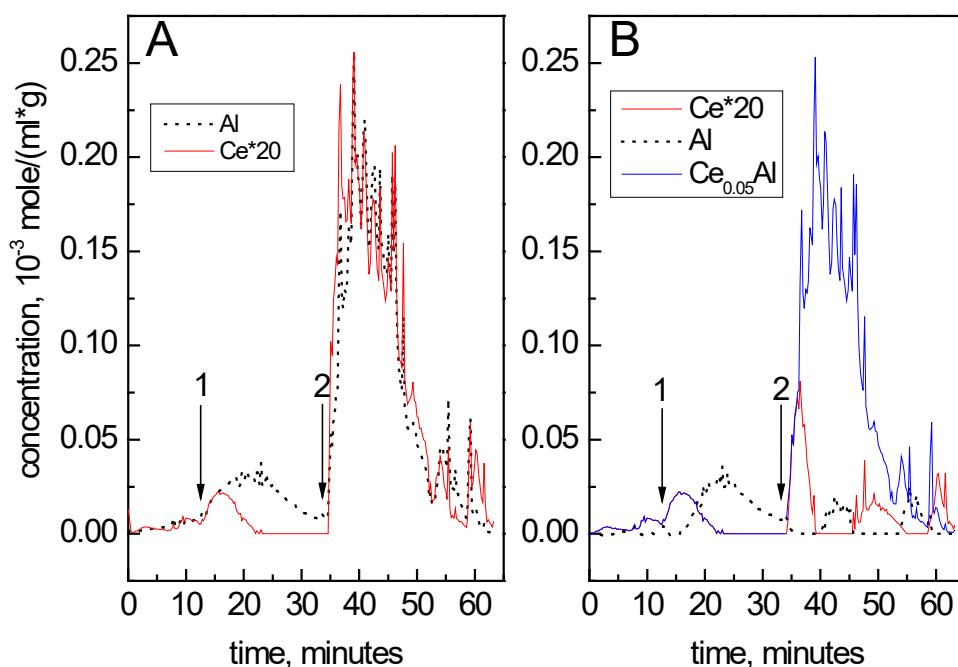
## Differential dissolution phase analysis (DDPA)

The general quantity of different compounds dissolved in (Ce+Al) sample in both HCl and HF containing flows (see Experimental Section) corresponded to 100% of Al and only 17% of Ce content therein (**Tables S1**). Complete dissolution of Al oxides agrees with absence of well crystallized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (**Table 1, Figure S1**) [1, 2]. There are several reasons that can be responsible for better dissolution of Ce containing compounds in the (Ce+Al) sample compared with that in pure CeO<sub>2</sub> calcined at the same temperature (~4%, [2]). They include smaller sizes of CeO<sub>2</sub> species (11 nm in (Ce+Al) and 68 nm in CeO<sub>2</sub>), presence of some X-ray amorphous ceria or penetration of some Ce into structure of Al oxides.

Kinetics of Ce and Al dissolution (**Figure S5A**) in this sample allows supposing formation of quite homogeneous mixed Ce-Al oxide with Ce<sub>0.05</sub>Al stoichiometry including ~80% of Al in the sample (**Figure S5B, Table 2**). Determined composition means that Ce in this oxide exists as preferentially isolated Ce<sup>3+</sup> ions. Ce-Al-O detection in HCl and HF could result from different morphology or disordering degree of the species with the same composition. More disordered species in turn can decorate alumina which follows from their consecutive dissolution in HCl. Alternate dissolution of some non-modified ceria or alumina in the temporal interval 40-63 minutes (HF flow) at constant registration of Ce-Al mixed oxide evidence their partial encapsulation by the last.

**Table S1.** Quantity of Fe, Ce, Al (as prepared, dissolved and insoluble) in different samples (mmol/g). Quantities of insoluble compounds were calculated from balance equations

Sample	As prepared			Dissolved			Insoluble compounds		
	Fe	Ce	Al	Fe	Ce	Al	Al	Ce	
Ce+Al	-	2.9	9.8	-	0.50	9.8	-	0	2.4
2.5Fe/(Ce+Al)	0.45	2.8	9.7	0.48	2.1	10.2	0	0	0.7
3.8Fe/Ce/Al	0.68	2.8	9.7	0.71	0.80	10.1	0	0	2.0



**Figure S5.** Differential dissolution curves of Ce and Al (A) and identified compounds (B) at stepwise consecutive change of flow composition from HCl (pH=2) to 1-3M HCl (1) and then to 3.6M HF (2) over (Ce+Al) sample.

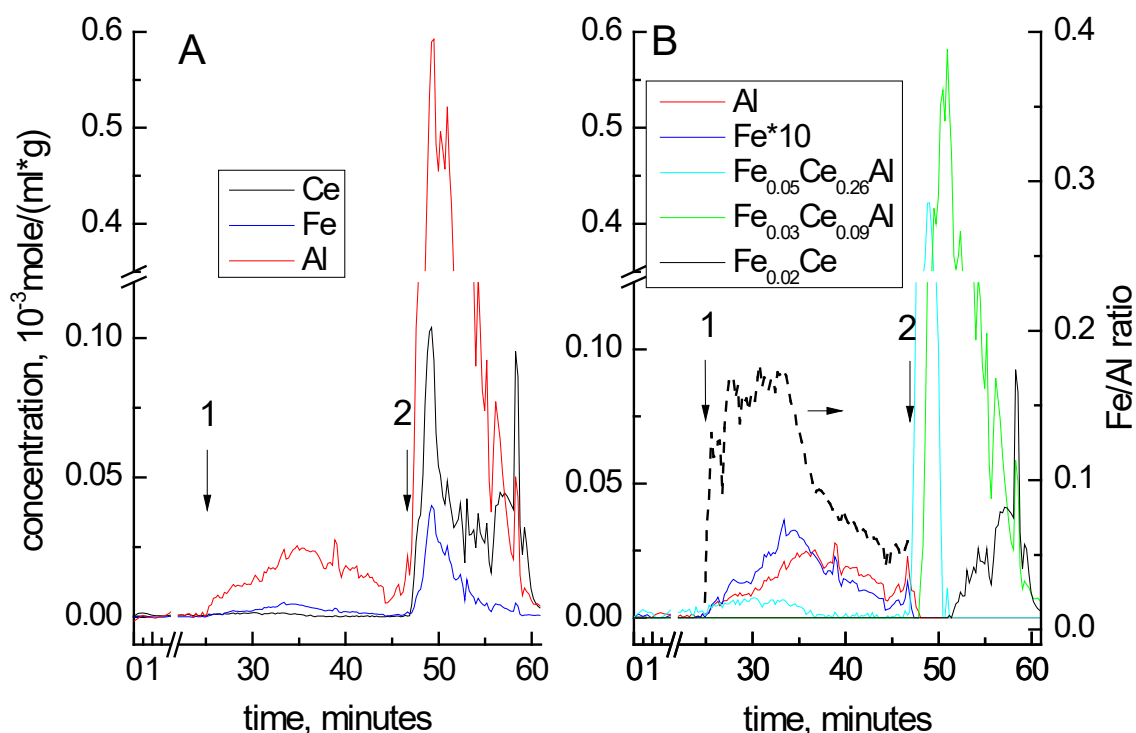
It is necessary to note substantial increase of solubility of Ce-containing compounds at complete dissolution of Al, Fe – containing compounds in the 2.5Fe/(Ce+Al) sample. So, only 0.7 mmol/g, or 25%, of Ce remained unsolved (**Table S1**). Earlier we observed similar effect for pure CeO<sub>2</sub> and related it to formation of Fe-Ce-O solid solution or mixed oxide [2]. Various compounds were identified by analysis the character of Fe, Ce

and Al dissolution curves at different periods of time in the 2.5Fe/(Ce+Al) sample (**Fig. S6A**).

Different dispersion or disordering degree of Ce-Al-O species with Ce<sub>0.05</sub>Al stoichiometry in the Ce+Al sample can affect the composition of Fe-Ce-Al mixed oxides formed in 2.5Fe/(Ce+Al) sample and dissolving in either HCl and immediately after switching to HF (with Fe<sub>0.05</sub>Ce<sub>0.26</sub>Al stoichiometry, totally 3.27 mmole/g), or exclusively in HF (with Fe<sub>0.03</sub>Ce<sub>0.09</sub>Al stoichiometry, 8.14 mmole/g) (**Figure S6B, Table 2**). Higher content of CeO<sub>2</sub> therein can be explained to continued and stimulated by Fe process of interaction of Ce-Al mixed oxide and CeO<sub>x</sub> during additional calcination after Fe supporting. At the same time, we cannot exclude that mixed oxides of such composition already formed in the (Ce+Al) sample, but only alumina containing fragments including some isolated Ce<sup>3+</sup> dissolved, while Fe insertion into ceria bulk resulted in their dissolution as well, like observed earlier for pure CeO<sub>2</sub> [2].

Some Fe-Ce mixed oxide (Fe<sub>0.02</sub>Ce stoichiometry) can be encapsulated by Fe-Ce-Al mixed oxide, like in the case of ceria capsulation by Ce-Al mixed oxide in the (Ce+Al) sample. It follows from dissolution of additional Fe and Ce in the temporal interval 51-61 minutes, while continuous registration of Fe, Ce and Al in Fe<sub>0.03</sub>Ce<sub>0.09</sub>Al stoichiometry took place (**Figure S6B**). Low Fe content in the detected Fe-Ce-O compound (Fe<sub>0.02</sub>Ce) explains absence of change of fluorite lattice parameter [3] (Table 1).

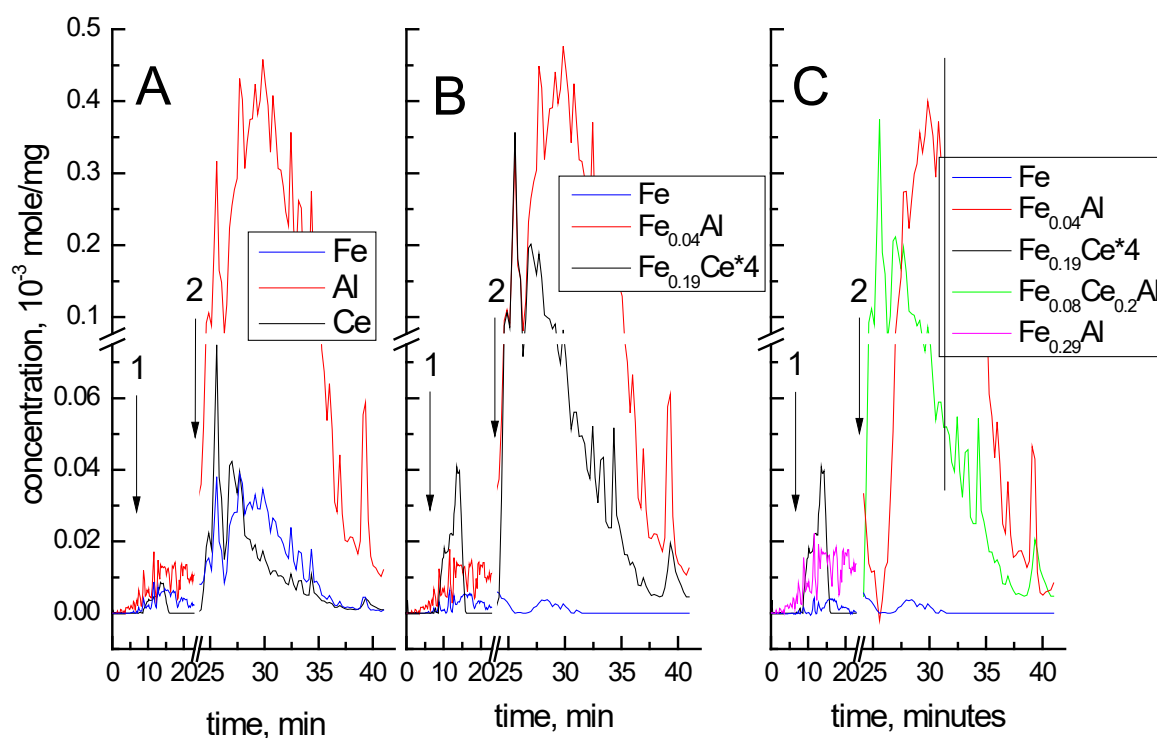
Some of residual Fe and Al detected in HCl (**Figure S6B**) obviously included into Fe-Al mixed oxide. Efficient penetration of Fe<sup>3+</sup> cations both into the lattice of  $\gamma$ -,  $\theta$ - Al<sub>2</sub>O<sub>3</sub> or the bulk of poorly crystallised alumina resulting in Fe-Al-O solid solutions or Fe-Al mixed oxide was already shown by DDPA and XRD [1, 2]. Larger Fe:Al ratio during dissolution in 1-3M HCl before 40 min can be due to both more efficient insertion of Fe<sup>n+</sup> ions into the most disordered near surface layers or smaller species of alumina or to the presence of some FeO<sub>x</sub> species on the surface of Fe-Al mixed oxide with Fe<sub>0.05</sub>Al stoichiometry. Its quantity (1.3 mmole/g) was reasonably close to that of alumina dissolving in HCl in the initial support (1.15 mmole/g) (Table 2).



**Figure S6.** Differential dissolution curves of Fe, Ce and Al (A) and identified compounds (B) at stepwise consecutive change of flow composition from HCl (pH=2) to 1-3M HCl (1) and then to 3.6M HF (2) over 2.5Fe/(Ce+Al) sample.

Noticeably lower quantity of Ce compounds dissolved in 3.8Fe/Ce/Al sample compared with 2.5Fe/(Ce+A) one (**Table S1**). First of all, it can be explained by higher sizes of  $\text{CeO}_2$  crystallites in the former of them (**Table 1**) inhibiting Fe penetration into ceria bulk. The correlation of kinetics of Fe concentration with either those of Ce or Al at different periods of dissolution in HF (**Figure S7A**) could point to presence of binary Fe-Ce and Fe-Al mixed oxides with corresponding stoichiometry  $\text{Fe}_{0.19}\text{Ce}$  and  $\text{Fe}_{0.04}\text{Al}$  (**Figure S7B**) and preferentially surface location of the former. The most disordered (or dispersed) of them dissolved in HCl. At the same time, like in 2.5Fe/(Ce+Al) sample, good correlation between  $\text{Fe}_{0.19}\text{Ce}$  and  $\text{Fe}_{0.04}\text{Al}$  curves observed in the initial period after HF supply (24-27 minutes) can be due to formation of Fe-Ce-Al mixed oxide with  $\text{Fe}_{0.08}\text{Ce}_{0.2}\text{Al}$  stoichiometry that screens Fe-Al mixed oxide (**Figure S7C**). Better penetration of Fe into the surface or more disordered layers of alumina is reasonable as

well. It can result in Fe-Al oxide with of  $\text{Fe}_{0.29}\text{Al}$  stoichiometry (dissolves in HCl) instead of  $\text{Fe}_{0.04}\text{Al}$  (dissolves in HF) (**Figure S7C, Table 2**).



**Figure S7.** Differential dissolution curves of Fe, Ce and Al (A) and initially (B) and finally (C) identified Fe-Ce-Al compounds at stepwise consecutive change of flow composition from HCl (pH=2) to 1-3M HCl (1) and then to 3.6M HF (2) over 3.8Fe/Ce/Al sample.

## References

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