

Response to the Comments from Reviewer 2#

Thank you for the valuable comments. We have considered all of your comments and revised our manuscript with respect to your suggestion. Your valuable suggestions and comments were carefully considered during the manuscript revision. All changes performed according to comments from Reviewer 1# and Reviewer 2# are highlighted using red word in the text. In addition, words rephrased according to similarity report are highlighted using blue word in the text.

REVIEWER REPORT(S):**Reviewer 2****Comments and Suggestions for Authors**

The subject of the manuscript is interesting and the authors performed a lot of experiments using advanced characterization techniques. However, before being accepted for publication the authors should improve their manuscript by considering the following aspects:

1) In the introduction section**Comment 1**

In the introduction section they should highlight more the practical importance of their study, as well as the economic advantages brought by the utilization of this type of membrane (CoSiOAlmemb)

Answer to Comment 1

Thank you for this valuable suggestion. In the revised manuscript, the following sentences were added:

Lines 74-76 in the revised manuscript,

for the purpose of developing novel hydrogen production, storage and transportation systems essential for the establishment of hydrogen-based society.

Comments 2, 7 and 8

line 64 - "heart" - replace by heat

line 286 - heart-treated - change to heat-treated

line 451 H₂-triggard chemical - I think it is H₂-triggered chemical

Answer to Comment 2, 7 and 8

We made all revisions in the revised manuscript.

2) In the experimental section**Comment 3**

(1) line 75 - ratio Co/Si = 1/8, 4/1, and 1/2 I think that it is 1/4 instead of 4/1

(2) line 76 - rephrase "according to a procedure reported elsewhere" or "according to a previously reported procedure"

(3) line 94 and 106 - rephrase "by following the published procedure" - using the previously published procedure

(4) line 99 - "to afford γ -Al₂O₃ thin layer over SiO₂ substrate" -rephrase "to afford the formation of γ -Al₂O₃ thin layer over SiO₂ substrate"

(5) line 100, line 135 - replace "under" by using

(6) line 141 - power - powder

Answer to Comment 3

In the revised manuscript, we made revisions and rephrased according to the valuable suggestions from

Reviewer 2#. Then, we made another revision: **Line 199** - power – powder.

Comment 4

lines 146-151 The authors describe the analysis performed in order to investigate the reversible redox property of Co cation in CoSiOAlpow2 when the treatment with H₂ was performed up to 350°C using Ar as inert gas.

- (1) Meanwhile at lines 182-189 it is described that in the case of the sample CoSiOAlpow the TPR was performed from 100 up to 500 °C using H₂/Ar mixture, then the sample was maintained 1 h under H₂ flow ? was it pure H₂ in this case or the same H₂/Ar mixture?

Answer to Comment 4 (1)

During the TPR measurement, The CoSiOAlpow sample was maintained under pure-H₂ flow at 500 °C for 1h. Thus, in **experimental section Line 209** in the revised manuscript, the word “H₂” was revised as “**pure-H₂**”.

- (2) Why the authors did not consider to perform also for this sample the same test as for the sample CoSiOAlpow2?

Answer to Comment 4 (2)

Thank you for this valuable comment. Indeed, we performed the cyclic TPR/TPD measurement for CoSiOAlpow2 sample. However, we could not identify the signal (H₂ consumption and desorption).

In the case of heterogeneous **CoSiOAlpow** sample, the Co cations are located at the SiO₂/γ-Al₂O₃ hetero interface, and thus the hydrogenation/dehydrogenation reactions proceed at once, which manage to make it possible to detect as H₂ consumption/desorption peaks for the hydrogenation/dehydrogenation reactions in the TPR/TPD profiles as shown in Figure S2.

On the other hand, in the case of the homogeneous **CoSiOAlpow2** sample, the hydrogenation reaction proceeds stepwise at each local active site where Co³⁺ is located, which leads to the gradual H₂ consumption that is not detectable as a distinct H₂ consumption peak in the TPR profile. Analogously, it is impossible to detect the H₂ desorption peak in the TPD profile for the CoSiOAlpow2 sample.

Section 3 Results and discussion

Comment 5

The authors do not mention anything about the chemical composition of the sample CoSiOAlmemb (which are the ratios Al:Si:Co in this case?)

Answer to Comment 5

Thank you again for this valuable suggestion. In the revised manuscript, the “Co/Si = 1/4” was added to explain the membrane synthesis procedure described in the experimental section 2.1 (3) of the original manuscript:

Lines 390-391 in the revised manuscript:

In this study, **the initial Co content of the SiO₂ layer was reduced from Co/Si = 1/2 to 1/4, then** the Co-doped SiO₂ layer (**Co/Si = 1/4**) was placed between the two mesoporous γ-Al₂O₃ layers to investigate the relationship between the Co(III)/(II) redox reactions at the SiO₂/γ-Al₂O₃ hetero interface and gas permeation properties.

As shown in Figures 9(a) and 9(b), this synthetic strategy led to the successful detection of H₂-triggered



chemical valve property. In the case of $\text{Co/Si} = 1/2$, the chemical valve property was also detected but, the time dependence shown in Figure 9(b) was something obscure. This is also the research topic we will investigate in the next step to optimize the H_2 -triggered chemical valve property.

Comment 6

The authors state at lines 336-339 "For further investigation on the redox reactions of Co cation species which proceeded around 250 to 350 °C, we prepared another powder sample with homogeneous structure and higher Co content labelled CoSiOAlpow2." However if one calculates the atomic content considering the preparation presented in the experimental section (ratio Al:Si:Co=8:8:1) it gives 6% Co instead of 5% which is in the case of Al:Si:Co=85:10:5) I do not think that a so little rise of the Co amount will be significant for their purpose. Also I think that the fact that this sample has equal amounts of Al and Si may have an influence on the obtained results.

Answer to Comment 6

Thank you again for this valuable comment. For XPS analysis to evaluate the oxidation state of Co in the aluminosilicate matrix, the Co/Al ratio of 1/17 in the Al:Si:Co=85:10:5 was increased to 1/8 in the homogeneous sample (Al:Si:Co=8:8:1) so as to detect the change in the oxidation state of Co clearly, and successfully detected as shown in Figure 7.

We should explain more carefully, and the text was revised as follows:

Lines 350-352 in the revised manuscript:

we prepared another powder sample labelled **CoSiOAlpow2** with homogeneous structure **having almost same Co content but higher Co/Al of 1/8 compared with that of CoSiOAlpow (1/17).**

Sincerely yours,

Yuji IWAMOTO

On behalf of all co-authors

Nagoya, Japan, November 17th, 2020.