Supplementary Materials

Propane dehydrogenation over cobalt aluminates: Evaluation of potential catalytic active sites

A.N. Chernov, S.V. Cherepanova, E.Yu. Gerasimov, I.P. Prosvirin, G.A. Zenkovets, A.A. Shutilov, K.Yu. Koltunov* and V.I. Sobolev*

*koltunov@catalysis.ru; *visobo@catalysis.ru

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Table S1. Grid parameters (a), average crystallite sizes and weight ratios.*

Catalyst	Average (a), Å	Co_3O_4 (a), Å	$\gamma\text{-}Al_2O_3$ (a), Å	Co_3O_4 D, nm	$\gamma\text{-}Al_2O_3$ D, nm	Co_3O_4 wt.%	$\gamma\text{-}Al_2O_3$ wt.%
CoAl-0.5	8.08(1)	8.08(1)	7.94(1)	10	11	54	46
CoAl-0.25	-	8.08(1)	7.95(1)	7	6	21	79
CoAl-0.25-R	-	8.08(1)	7.96(1)	9	7	29	71
CoAl-0.1	7.99(1)	8.08(1)	7.95(1)	5	5	11	89
CoAl-0.1-R	7.97(1)	8.08(1)	7.95(1)	5	6	5	95
CoAl-0.05	7.96(1)	8.08(1)	7.94(1)	5	5	9	91
Co/Al_2O_3	-	8.08(1)	7.92(1)	5	7	13	87

* The average lattice parameter (a) was defined for those samples where the Co_3O_4 peak and the $\gamma\text{-}Al_2O_3$ peak overlapped to form one more or less symmetric peak. The grid parameter (a) for Co_3O_4 can only be determined for CoAl-0.5, for the other catalysts it was fixed at this value.
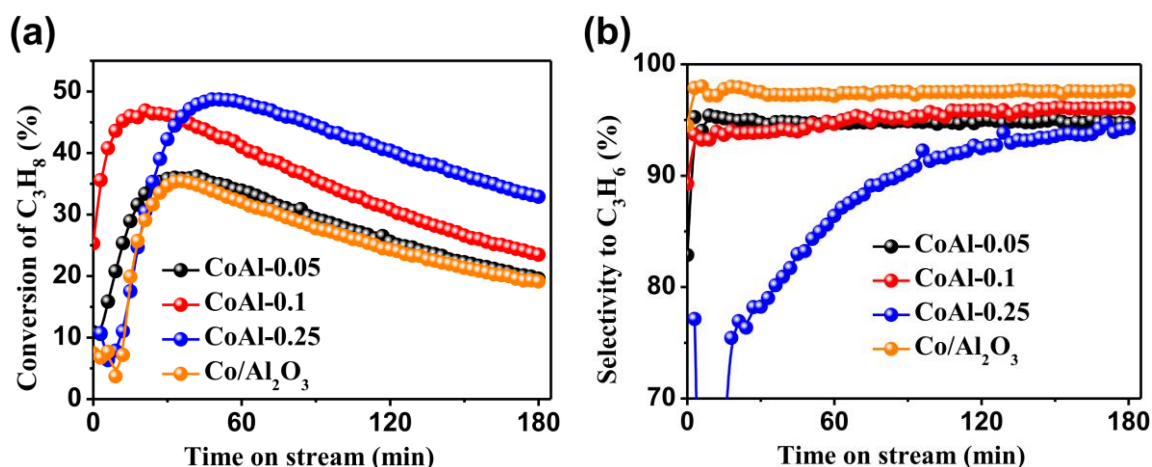

Figure S1. Propane conversion (**a**) and selectivity to propylene (**b**) as functions of time on stream over CoAl and Co/Al_2O_3 catalysts at $T = 600$ °C and $P = 1$ atm. Gas mixture: 10 vol.% propane, N_2 balance; GHSV = 7500 ml h^{-1} g$_{cat}$$^{-1}$.
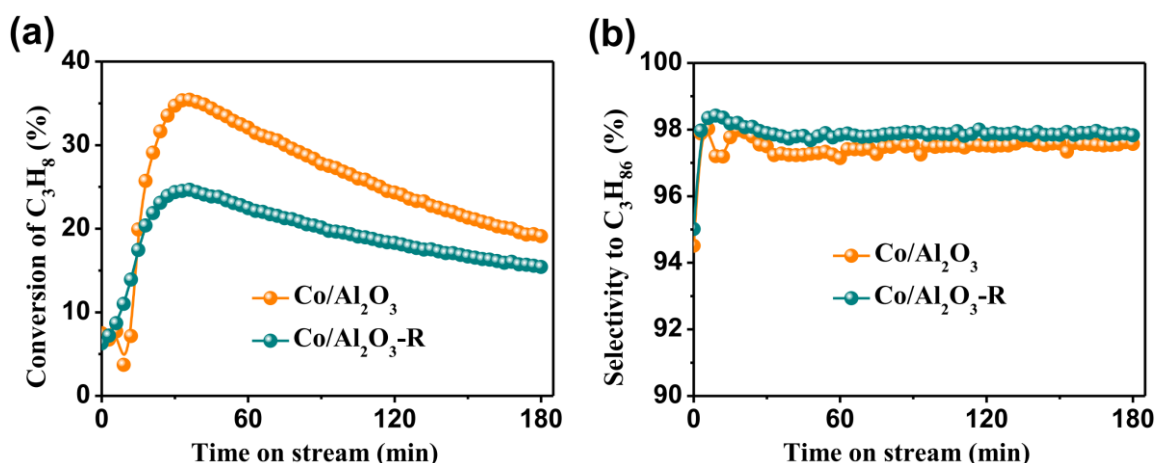

Figure S2. Propane conversion (**a**) and selectivity to propylene (**b**) as functions of time on stream over Co/Al_2O_3 and Co/Al_2O_3-R catalysts at $T = 600$ °C and $P = 1$ atm. Gas mixture: 10 vol.% propane, N_2 balance; GHSV = 7500 ml h^{-1} g$_{cat}$$^{-1}$.
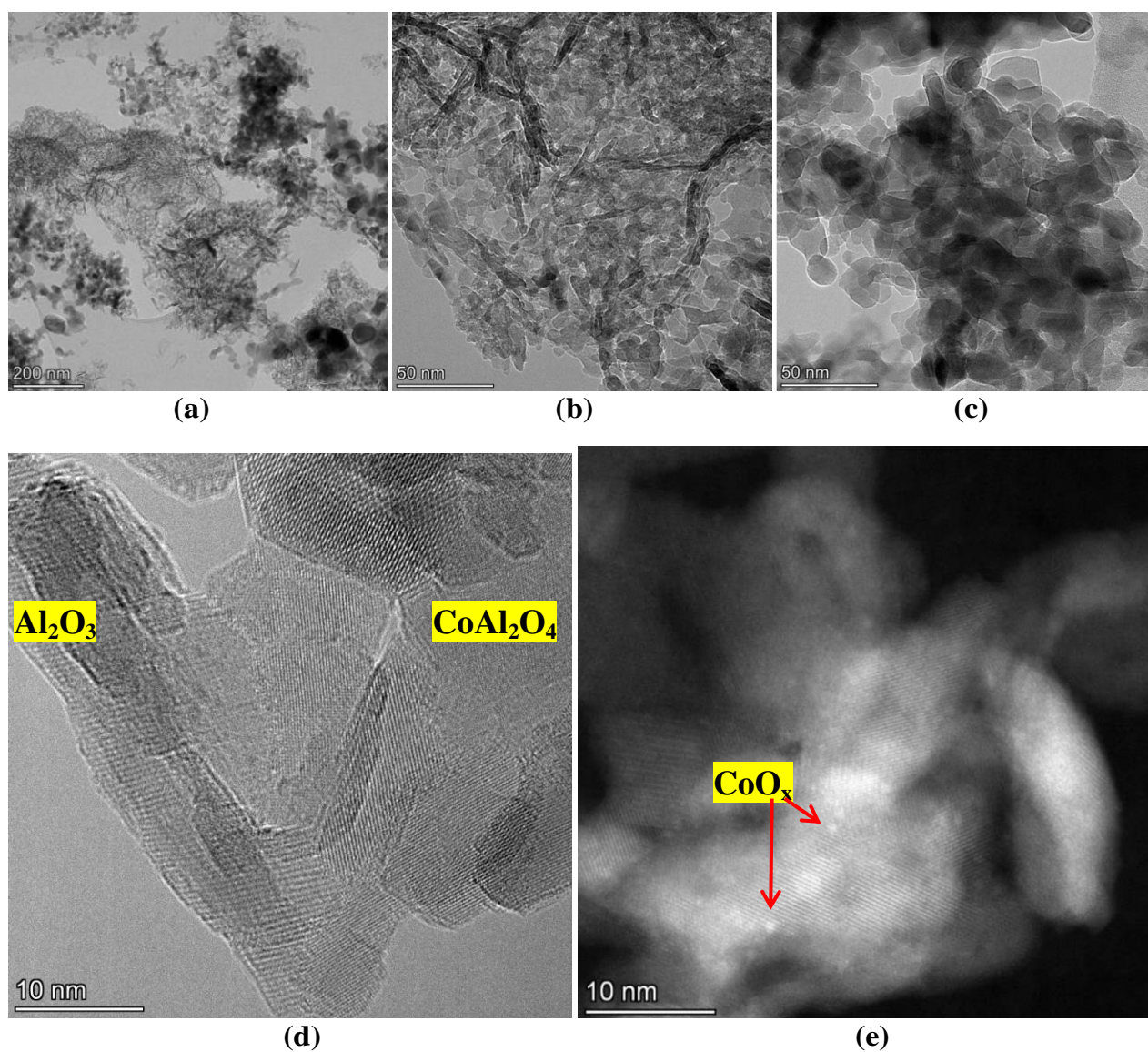
Figure S3. Low (**a**) and higher (**b–d**) magnification TEM images of the spent-regenerated CoAl-0.25-R catalyst, confirming significant differentiation in its morphology, namely the presence of separate phases of crystalline alumina, cobalt aluminate and cobalt oxides. (**e**) HAADF-STEM image of Al_2O_3 area in CoAl-0.25-R, showing CoO_x particles embedded on its surface.
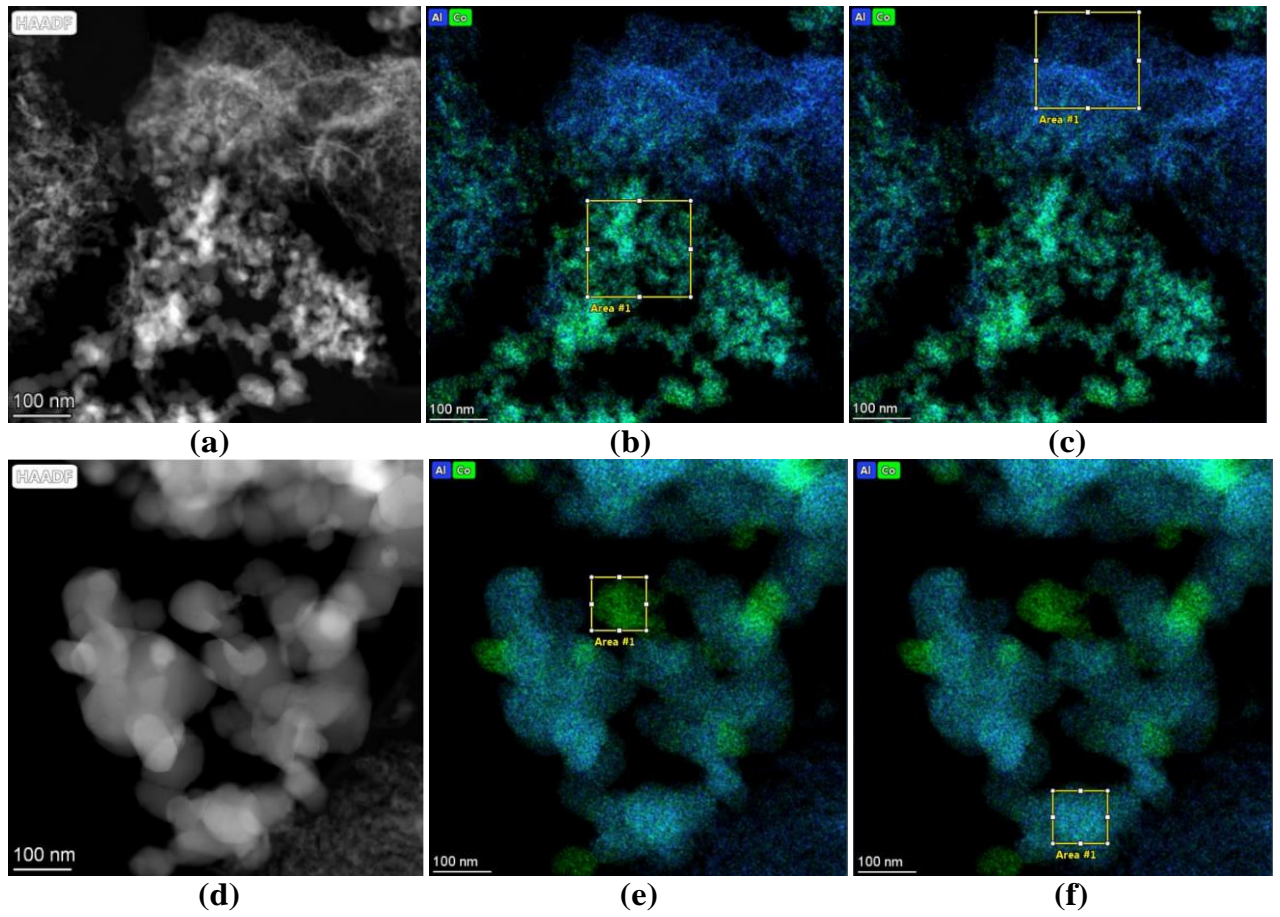
(a)   **(b)**   **(c)**

(d)   **(e)**   **(f)**

Table 1. Analysis of spectrum from Area #1 in (b).

Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
8	O	K	61.95	6.96	41.21	2.88	0.16
13	Al	K	25.93	5.89	29.09	6.09	0.15
27	Co	K	12.12	2.11	29.69	4.47	0.19

Table 2. Analysis of spectrum from Area #1 in (c).

Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
8	O	K	59.57	8.72	43.80	3.95	0.35
13	Al	K	36.30	8.92	45.02	9.77	0.09
27	Co	K	4.13	0.82	11.18	1.80	0.34

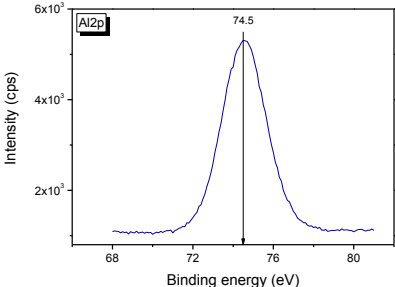**Table 3. Analysis of spectrum from Area #1 in (e).**
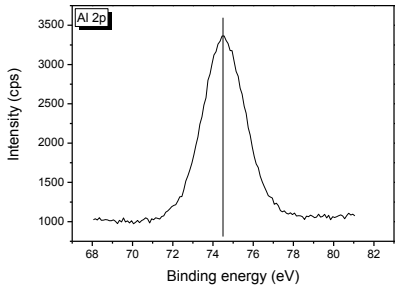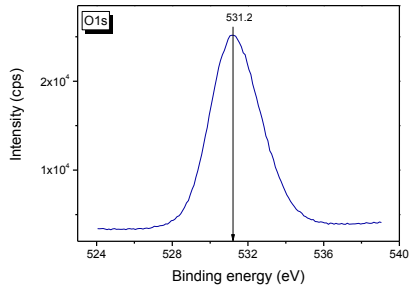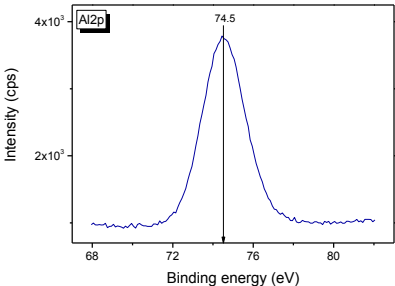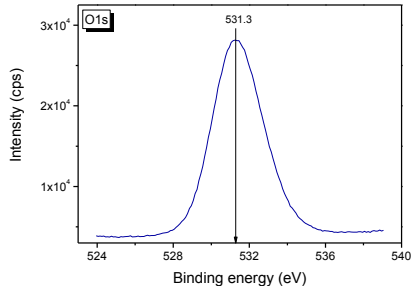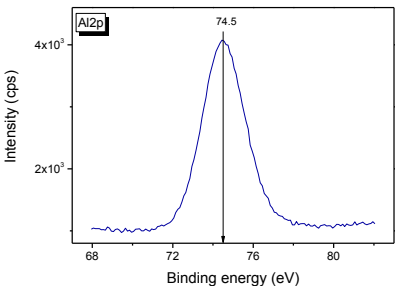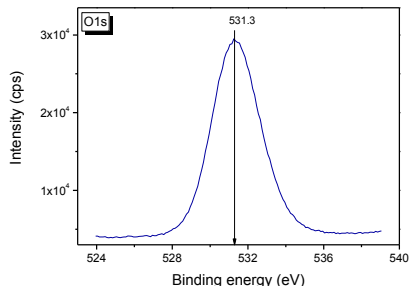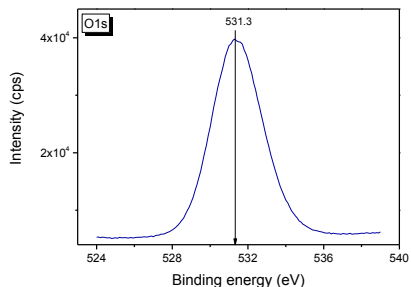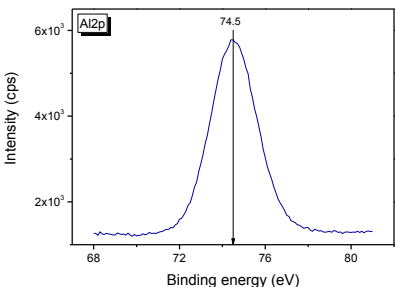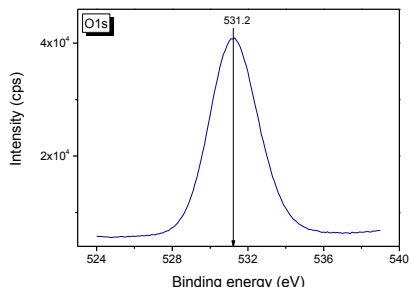
Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
8	O	K	61.72	8.61	30.67	2.83	0.74
13	Al	K	0.76	0.20	0.64	0.16	10.84
27	Co	K	37.52	7.24	68.69	11.14	0.89

Table 4. Analysis of spectrum from Area #1 in (f).

Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
8	O	K	58.64	6.91	37.29	2.73	0.68
13	Al	K	26.91	6.19	28.86	6.08	1.15
27	Co	K	14.45	2.57	33.85	5.14	0.24

Figure S4. (**a,d**) HAADF-STEM and related (**b,c,e,f**) EDX-STEM Co and Al elemental mapping images of different areas of CoAl-0.25-R, confirming significant differentiation in its morphology, namely the presence of separate phase close in composition to $CoAl_2O_4$ (Tables 1 and 4), Al_2O_3 (Table 2) and cobalt oxides CoO_x (Table 3).

Table S2. High resolution XPS spectra of Al 2p and O 1s of the samples.

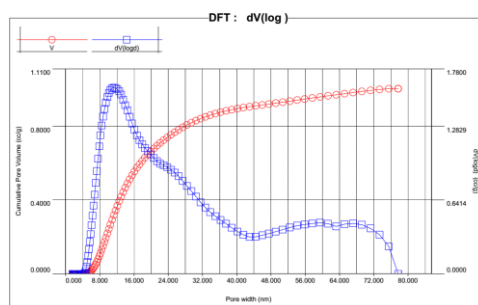| Catalyst	XPS spectra of Al 2p	XPS spectra of O 1s
CoAl-0.5		
CoAl-0.25		
CoAl-0.25-R		
CoAl-0.1		
CoAl-0.1-R		
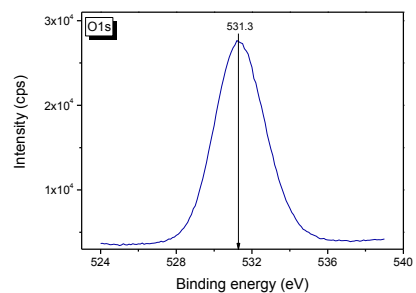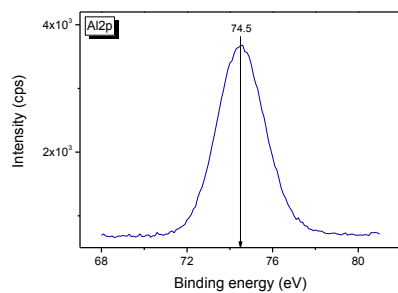
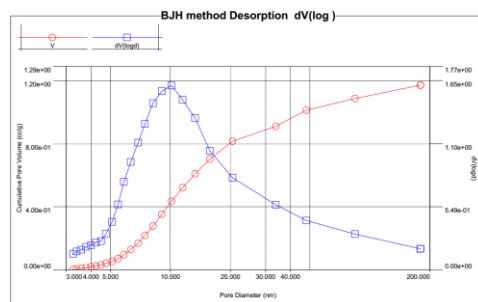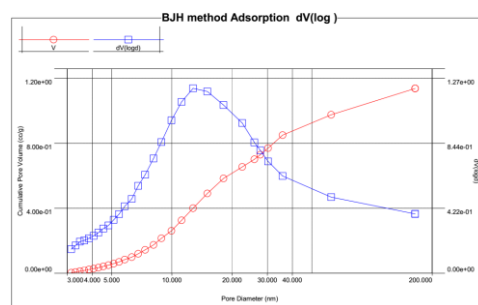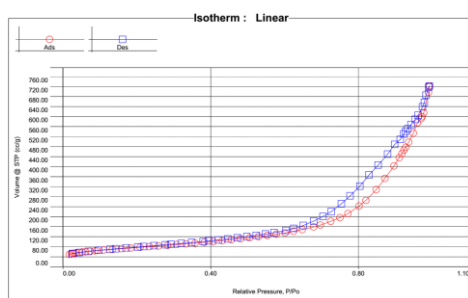| CoAl-0.05 | | |
| Co/Al$_2$O$_3$ | | |
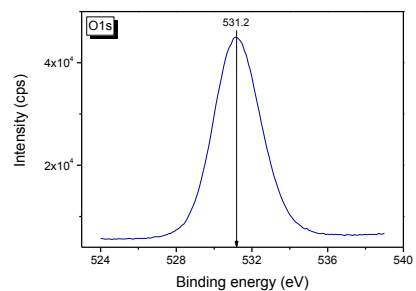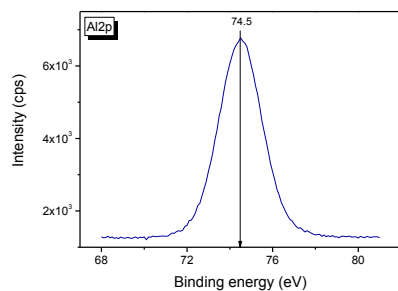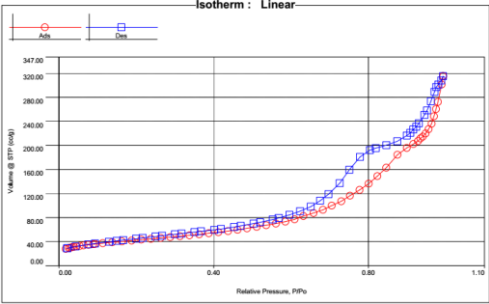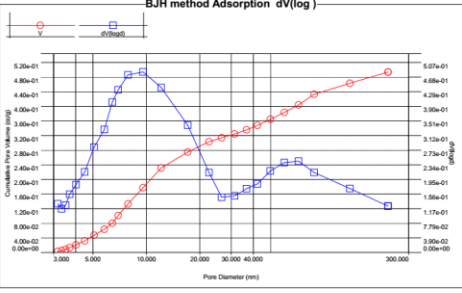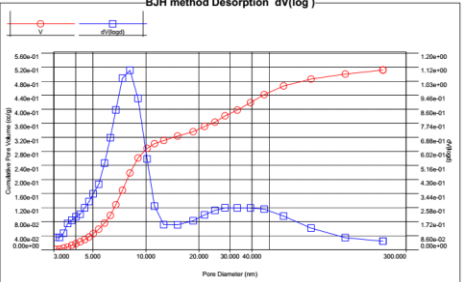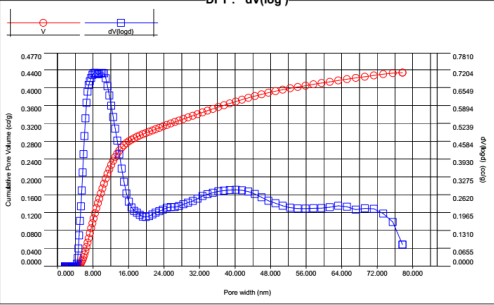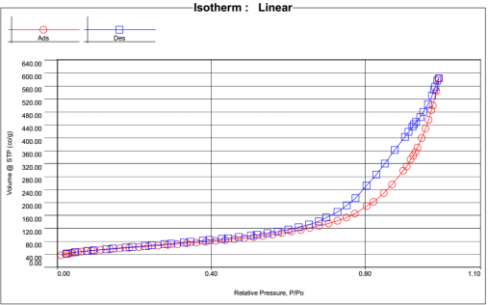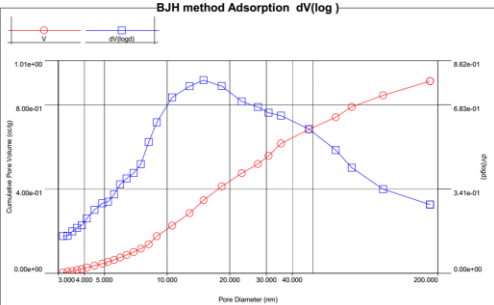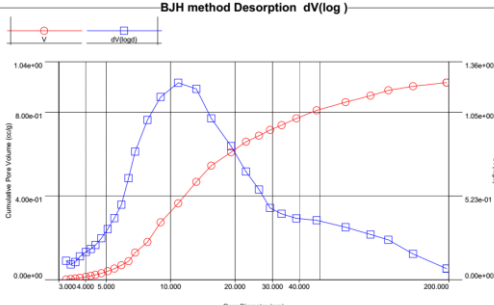
Table S3. The N_2 adsorption/desorption isotherms and the pore size distribution of the samples.

Catalyst	N_2 adsorption/desorption isotherms	Pore size distribution
CoAl-0.5		
CoAl-0.25		

CoAl-0.25-R		
CoAl-0.1		

| CoAl-0.1-R | | |

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CoAl-0.05		
Co/Al₂O₃		

Al₂O₃		