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Screening of Metal Oxides for Hg^0 Capture

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Abstract

Fossil fuel related industries are the major anthropogenic sources of Hg^0 emission. Due to awareness of the detrimental impact, there is an increasing interest in discovering potential materials for Hg^0 removal. In this paper, the first-row transition metals (from V to Zn), Mo and rare earth metals (La and Ce) in the oxidation states supported by γ-Al$_2$O$_3$ were prepared and studied as potential candidates for Hg^0 capture. Based on evolution of the parameters of enthalpies (ΔH), Gibbs free energy (ΔG), adsorption peaks ($T_{a, peak}$), maximum Hg^0 capture efficiencies (μ_{max}) and activation energy (E_a) etc, the samples of Cr, Ni, Fe, Mn, Co, Ce and Cu showed better performances for Hg^0 capture amongst the 11 metal oxides. The results also indicated that MoO$_3$ has potential to promote Hg^0 capture since the activation energy is relatively low. Consequently, most of the Mo-based binary metal oxides have relatively high Hg^0 removal efficiencies coupled with low activation energies. Particularly, the binary metal oxides of CrMo, MnMo, CuMo, CeMo and CoMo could be selected as appropriate candidates for Hg^0 capture within specific temperature windows.

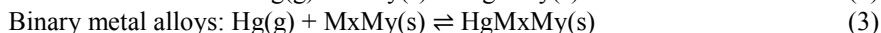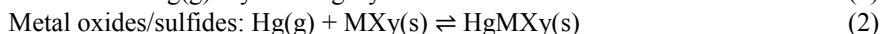Keywords: Hg^0 Capture; Metal oxides; Screening method; thermodynamic data; and kinetic parameters

1. Introduction

There has been a growing concern on the pollution by mercury due to its volatility, toxicity, persistence, and bioaccumulation in the environment [1, 2]. Coal combustion/gasification power plants [2, 3], cement and mineral production plants [1] and petrochemical refineries [4] are the major anthropogenic sources of mercury emission. The emitted mercury leads to detrimental impacts on biological systems including potential lethal effects on human health, especially on fetal development during pregnancy. The

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mercury compounds are generally emitted in three forms: elemental (Hg^0), oxidized (Hg^{2+}), and particle-bound ($Hg^{(p)}$). Amongst them, Hg^0 appears to be most dominant. It is extremely difficult to remove Hg^0 since it is highly volatile in air and insoluble in water [5]. The removal of Hg^0 often requires surface oxidation (at lower temperatures) because the oxidized form (Hg^{2+}) is more reactive and relatively easier to capture [2]. In recent years, cost-effective technologies for Hg^0 capture have become increasingly important due to the ever-tightening legislations for emission control. As a consequence, there is a considerable interest in screening and thus narrowing down the potential materials for Hg^0 removal.

In order to address the needs, computational chemistry is a commonly used method to screen materials more quickly and inexpensively than experimental methods [6]. It is believed that reaction kinetics, surface effects, particle size, residence time, mass transfer limitations and interactions with other gas constituents are only secondary effects if the material is not thermo-dynamically capable of adsorbing Hg^0 [6-8]. 22 pure metals [7], 23 metal oxides/sulfides [6] and 17 binary metal alloys [8] as potential candidates were evaluated by reaction enthalpies (as below) via density functional theory (DFT) calculations.

Pure metals: $Hg(g) + yM \rightleftharpoons HgM_y$ (1)

Metal oxides/sulfides: $Hg(g) + MX_y(s) \rightleftharpoons HgMX_y(s)$ (2)

Binary metal alloys: $Hg(g) + M_xM_y(s) \rightleftharpoons HgM_xM_y(s)$ (3)

(Where, x and y are stoichiometric coefficients, M refers to a pure metal and X refers to an oxide or a sulfide)

Despite the fact that thermochemical property was identified as a chief indicator to evaluate the candidate materials, Hg^0 capture process may not follow the predicted reactions, and surface reaction kinetics could be enhanced by catalytic effects with the lowering of activation energy. In this paper, we propose a reliable methodology with a combination of computational calculations and experimental investigations to evaluate candidate materials for Hg^0 capture at different temperatures.

2. Materials & methods

2.1. Preparation of metal oxides

The first-row transition metals (from V to Zn), Mo and rare earth metals (La and Ce) were selected as metal precursors for preparation of samples. The metal salts used were NH_4VO_3, $Cr(NO_3)_3 \cdot 9H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, respectively (analytical grade, Sinopharm Chemical Reagent Co, Ltd.). The metal oxides (10 wt.%) samples were prepared by incipient wetness impregnation (IWI) of commercial γ-Al_2O_3 support (V-SK Co., Ltd., size range of $1.18 \leqslant x \leqslant 1.70$ mm, surface area of 188 m² /g) with the solution of the 11 salts followed by drying at 120 °C for 24 h and calcination at 520 °C for 12 h in air. The binary metal oxides were prepared after the Mo metal oxides (20 wt.%) were produced with similar method.

2.2. Temperature-programmed surface reaction

A temperature-programmed surface reaction (TPSR) with bare surface method [9] was applied to study the characteristics of Hg species capture/desorption processes. Samples (2 g) were loaded into two fixed-bed reactors in parallel (one as reference for temperature detection), the inner diameter, of which is 12 mm. Teflon pipes and quartz reactors were chosen to avoid adsorption of mercury onto piping line and equipment. The gas phase Hg^0 (around 30 μg/m³) in N_2 with a flow rate of 1500 ml/min, supplied by mercury generator (Tekran 2537, USA), was introduced into the reactor. Both Hg^0 and Hg^{2+} were

measured continuously during the TPSR experiments using an online mercury analysis system (Tekran 3300RS, USA). The instrument was calibrated and the bypass concentration (i.e. baseline concentration) was checked by the mercury generator before each experiment. The test samples were heated from 25°C to 700°C at a heating rate of 1°C/min.

3. Results & discussions

3.1. Metal oxides

Table. 1. Thermodynamic results of the 11 metal oxides

Sample[a]	Stable phase[b]	Thermodynamic data[c]	
		ΔH (kJ/mol)	ΔG (kJ/mol)
V	V_2O_5	-6.83E+02	-1.58E+02
Cr	Cr_2O_3	-7.13E+02	-1.64E+02
Mn	MnO_2	-3.20E+04	-9.44E+03
Fe	Fe_2O_3	-1.13E+02	-3.92E+01
Co	Co_3O_4	-1.17E+02	-4.01E+01
Ni	NiO	-1.06E+02	-3.74E+01
Cu	CuO	-1.23E+02	-4.15E+01
Zn	ZnO	-9.41E+01	-3.45E+01
Mo	MoO_3	-3.93E+02	-1.00E+02
La	La_2O_3	-9.66E+01	-3.51E+01
Ce	CeO_2	-1.02E+02	-3.64E+01

a, Impregnated over γ-Al_2O_3. b and c, Computationally calculated using FactSage 6.3 with Phase Diagram and Equilib module, respectively.

The first-row transition metals (from V to Zn), Mo and rare earth metals (La and Ce) in oxidation states supported by γ-Al_2O_3 were used as potential candidates for Hg^0 capture. The stable phase of metal oxides predicted and the related thermodynamic parameters using the reactions of the metal oxides with Hg^0 are summarized in Table 1. These results were calculated using FactSage 6.3 with the Phase Diagram module at the samples calcination conditions and Equilib module at the conditions of the metal oxides achieving maximum efficiencies (i.e. $T_{a, peak}$ in Table 2), respectively. Reactions of listed stable metal oxides with gas phase Hg^0 are exothermic spontaneous reactions since both the ΔH and ΔG values are negative. However, ΔG of the reactions with Hg^0 are various. According to the minimum Gibbs free energy theory, the reaction effective levels follow the order of ΔG values, i.e. Mn < Cr < V < Mo < Cu < Co < Fe < Ni < Ce < Zn < La.

Table. 2. Summary of reaction kinetics for the 11 metal oxides

Sample[a]	T_{a0}	$T_{ra, peak}$	$T_{a, peak}$	μ_{max}	T_{d0}	$T_{rd, peak}$	$T_{d, peak}$	$R_{d/a}$	E_a	r^2
	°C	°C	°C	%	°C	°C	°C	%	kJ/mol	-
V	<25	47	96	45	213	213	423	31.74	11.26	0.9982
Cr	<25	<25	92	89.4	356	366	474	62.27	0.40	0.9952
Mn	77.5	235	260	82.7	330	340	383	99.75	41.83	0.9908
Fe	176	275	360	86.3	436	465	475	97.59	106.37	0.9966
Co	192	270	353	77.5	423	440	462	89.93	81.39	0.9978
Ni	239	314	377	89	454	493	502	97.49	100.76	0.9977
Cu	237	201	342	57.2	386	452	464	97.49	50.92	0.9737
Zn	329	380	407	21.3	455	455	492	76.03	154.25	0.9865
Mo	31	116	154	18.5	198	201	246	99.42	38.67	0.9920
La	346	386	400	12.7	467	475	506	92.13	108.61	0.9856
Ce	211	287	386	61.3	427	439	456	98.19	69.37	0.9915

Correspondingly, the temperature-programmed surface reaction (TPSR) was selected as an experimental method for screening of the γ-Al$_2$O$_3$ supported metal oxides. Negligible effect of Hg^0 (approximately 30 μg/m^3) was recorded between 25°C and 600°C when the support γ-Al$_2$O$_3$ was tested. However, the γ-Al$_2$O$_3$ loaded with metal oxides showed different behaviours in terms of adsorption and desorption with increasing temperatures. For the TPSR profiles, each metal oxide experienced characteristic temperatures (in an increasing order) of initial adsorption (T_{a0}), adsorption rate peak ($T_{ra, peak}$), adsorption peak ($T_{a, peak}$), initial desorption (T_{d0}), desorption rate peak ($T_{rd, peak}$) and desorption peak ($T_{d, peak}$). These temperatures are summarised in Table 2.

The initial adsorption temperatures (T_{a0}) of Hg^0 capture for the first-row transition metals increased from 25 to 329°C with the increase in atomic number (from V to Zn). The Mo sample started to show significant efficiency at around 30°C whilst La and Ce at 346°C and 211°C, respectively.

The temperatures of $T_{a, peak}$, between that of $T_{ra, peak}$ and T_{d0}, could be selected as the effective temperatures for Hg^0 capture with the maximum efficiencies (μ_{max}). It is observed that the $T_{a, peak}$ and μ_{max} for each sample are different, and thus unique to each sample. The maximum efficiencies (with $T_{a, peak}$) are in the order of Cr (89.4% at 92°C) > Ni (89% at 377°C) > Fe (86.3% at 360°C) > Mn (82.7% at 260°C) > Co (77.5% at 353°C) > Ce (61.3% at 386°C) > Cu (57.2% at 342°C) > V (45% at 96°C) > Zn (21.3% at 407°C) > Mo (18.5% at 154°C) > La (12.7% at 400°C). Amongst them, the samples of Cr, Ni, Fe, Mn, Co, Ce and Cu showed better activity for Hg^0 capture.

The outlet concentration of Hg^0 for each sample is higher than the baseline concentration (30 μg/m^3) after the temperature of T_{d0}. This is followed by a peak at a certain temperature ($T_{d, peak}$). The temperatures of $T_{d, peak}$ and after the $T_{rd, peak}$ could be important parameters when the regenerations of sample are considered. All of the $T_{d, peak}$ occurred at temperatures higher than 380°C. However, that of Mo occurred at a relatively low temperature (246°C). Furthermore, the ratio of absorbed and desorbed amount of Hg^0 ($R_{d/a}$) was calculated by taking into account the absolute areas above and below the baseline concentration of Hg^0. The ratios were above 90% for most of the samples (except for V, Cr and Zn). The Hg^0 could be captured in HgO form at the O side of the metal oxides whilst the chemically adsorbed Hg^0 desorbs with increasing temperatures. The reaction enthalpies have been used as an indicator to screen materials for Hg^0 capture with the predicted reactions [6-8]. In this research, nevertheless, the results proved that Hg^0 capture processes do not follow the predicted reactions.

In order to further study the chemisorption process, activation energy (E_a) was calculated, which is an important factor to evaluate the candidates. The value of E_a can be obtained from the Arrhenius plotting of the results (ranging from T_{a0} to $T_{ra, peak}$) from the differential analysis of TPSR experimental data. The calculated E_a (with high r^2 values) are in the order of Cr < V < Mo < Mn < Cu < Ce < Co < Ni < Fe < La < Zn, which are almost consistent with that of thermodynamic study.

3.2. Binary metal oxides

Based on the evaluation of the 11 metal oxides, Cr, Mn, Fe, Co, Ni, Cu and Ce were selected as precursors (whilst Mo as promoter) to prepare binary metal oxides as listed in Table 3. The predicted exothermic spontaneous reactions showed lower ΔG values when compared with each individual precursors and the values were in the increasing order of MnMo < CuMo < CrMo < CoMo < CeMo < NiMo < FeMo.

Table. 3. Thermodynamic results of the 7 binary metal oxides

Sample[a]	Stable phase[b]	Thermodynamic data[d]	
		ΔH(kJ/mol)	ΔG(kJ/mol)
CrMo	Cr_2O_3, MoO_3	-1.57E+03	-3.37E+02
MnMo	MnO_2, MoO_3	-7.73E+04	-2.81E+04
FeMo	Fe_2O_3, MoO_3	-1.41E+02	-4.59E+01
CoMo	Co_3O_4, MoO_3	-1.95E+02	-5.83E+01
NiMo	NiO, MoO_3	-1.55E+02	-4.90E+01
CuMo	CuO, MoO_3	-1.04E+04	-1.74E+04
CeMo	CeO_2, MoO_3	-1.60E+02	-5.04E+01

a, Impregnated over γ-Al_2O_3. b and c, Computationally calculated by FactSage 6.3 using the Phase Diagram and Equilib module, respectively.

The TPSR experiments were conducted in order to further study the 7 selected binary metal oxides as potential candidates and the results are presented in Table 4. The reaction kinetic parameters listed in Table 4 show that the addition of Mo phase has positive effects on Hg^0 capture. Specifically, the values of E_a are lower than that of the individual metal oxides and the reduced level are 37.50, 36.03, 35.40, 33.22, 28.30 and 20.02 kJ/mol for CoMo, CeMo, CuMo, MnMo, FeMo and NiMo samples, respectively. The E_a values of the binary metal oxides that are promoted by Mo are in the increasing order of CrMo < MnMo < CuMo < CeMo < CoMo < FeMo < NiMo. Particularly, the CrMo, MnMo and CuMo samples showed significant Hg^0 capture capability even at room temperature (25°C) and then achieved highest efficiencies at 25°C (96.8%), 256°C (94.2%) and 325°C (88.5%), respectively. The CeMo and CoMo samples showed relatively higher Hg^0 removal efficiencies of around 88% with lower activation energy. These results are also better than those for individual metal oxides.

Table. 4. Summary of reaction kinetics for the 7 binary metal oxides

Sample[a]	$T_{a, 0}$	$T_{ra, peak}$	$T_{a, peak}$	μ_{max}	$T_{d, 0}$	$T_{rd, peak}$	$T_{d, peak}$	$R_{d/a}$	E_a	r^2
	°C	°C	°C	%	°C	°C	°C	%	kJ/mol	-
CrMo	<25	<25	<25	>96.8	260	260	480	53.33	0	-
MnMo	<25	73	256	94.2	412	452	452	11.94	8.61	0.9965
FeMo	170	204	312	91.8	413	423	440	56.37	78.07	0.9439
CoMo	116	170	203	87.8	420	420	550	9.72	43.90	0.9944
NiMo	196	241	294	78.9	398	398	430	29.72	80.74	0.9970
CuMo	27	152	325	88.5	423	445	494	4.703	15.52	0.9945
CeMo	83	165	287	88.8	410	420	468	36.56	33.35	0.9927

By contrast, the calculated $R_{d/a}$ results are lower than that for each individual compound, which indicate that the reaction behaviours of these binary metal oxides on Hg^0 capture are different. Moreover, there were solid (HgO) products coated on the cooled part of the quartz reactor. These results suggest that the synergistic catalytic effects on oxidation of Hg^0 to Hg^{2+} may have taken effect for most of the Mo based binary metal oxide samples rather than just chemical adsorption and desorption process as with most of the individual metal oxides.

4. Conclusions

In this paper, we have developed a combination of computational calculation and experimental investigation methods and screened 11 metal oxides and 7 binary metal oxides supported on γ-Al_2O_3.

Both thermodynamic and reaction kinetic parameters, such as reaction enthalpies (ΔH), Gibbs free energy (ΔG), adsorption peaks ($T_{a, peak}$), peak capture efficiencies (μ_{max}) and activation energy (E_a), were

selected as indicators to evaluate the performance. The metal oxides of Cr, Ni, Fe, Mn, Co, Ce and Cu showed better activity for Hg^0 capture. Although the recorded efficiencies for MoO_3 were too low to be competitive, it has potential to promote the Hg^0 capture since the activation energy is relatively low.

Further results of 7 Mo-based metal oxides demonstrated that the additive of Mo has positive synergistic effects on both efficiencies and activation energies of the Hg^0 capture when compared with each individual metal oxide. Most of the prepared binary metal oxides showed Hg^0 removal efficiencies of over 80%. Therefore, they can be used as candidate materials for Hg^0 capture in different temperature windows.

Acknowledgements

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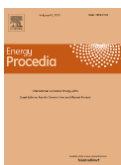
Biography

Dr Tao Wu is an Associate Professor and Reader in clean energy technologies at The University of Nottingham Ningbo China (UNNC). He has over 20 years of R&D experience on the efficient conversion and utilization of fossil fuels and biomass. He is currently leading the Ningbo Municipal Key Laboratory of Clean Energy Conversion Technologies at UNNC.