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Deactivation performance and mechanism of alkali (earth) metals on V_2O_5–WO_3/TiO_2 catalyst for oxidation of gaseous elemental mercury in simulated coal-fired flue gas

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ABSTRACT

Catalysis deactivation caused by alkali (earth) metals (Na, K, Mg and Ca) over V_2O_5–WO_3/TiO_2 catalyst for oxidation of Hg^0 by hydrogen chloride was investigated in the presence of O_2. Deactivation effects caused by alkali (earth) metals were well associated with alkalinity value and shown in sequence as: $K > Na \sim Ca > Mg$. Results also indicated that the deactivation increased proportionately with alkali (earth) metal doping amounts. Further investigations on BET surface area, XRD, Hg-TPD, XPS and H_2-TPR demonstrated that surface characteristics were not the dominant factor for the deactivation. However, surface coverage by alkali (earth) metals might cause decrease in the surface area and total pore volume. Hg-TPD results indicated that the doping of alkali (earth) metals would decrease surface Hg^0 adsorption amount associated with alkalinity value. More decrease of surface adsorption and redox ability (Oα) in doped catalysts than the fresh one could lead to less active performance according to the H_2-TPR and XPS of O 1s results. Consequently, the decrease of Hg^0 adsorption and surface redox ability (Oα), and the formation of inactive metavanadate species such as KVO_3 could be responsible for the deactivation performance caused by alkali (earth) metals over vanadium-based catalyst for oxidation of gaseous elemental mercury.

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1. Introduction

Studies of the occurrence of mercury oxidation in flue gas are critical for reasons associated with both the improved performances and successful control technologies over multi-effect catalysts [1–4]. The most important catalysts currently used for air pollutant removal such as NOx are based on V_2O_5–WO_3/TiO_2 while it has been proven to be one of the most effective catalysts for reducing both Hg^0 and NOx in coal-fired flue gas [5]. It is reported that vanadium is an active phase, while tungsten is considered as a promoter that stabilizes the anatase form of titania, which favors the spreading of the vanadium onto the catalyst surface, and increases the acidity of the catalyst [6,7]. Although a thermodynamic evaluation to the oxidation of Hg^0 over vanadium–(tungsten)–titanium catalyst indicates a high reactivity under ideal conditions based on its effectiveness and probable practical applications [8,9], no fundamental studies on the poisoning effects of the catalysts have been carried out for the removal of Hg^0, which totally hinders our awareness and understanding toward it. To establish high performance and reliability before application in a real power plant, it is necessary to investigate a catalyst and understanding the reaction process correlated with anti-poison ability to several compounds such as alkali and alkaline earth oxides.

Fine fly ash is a major concern for catalysts in flue gas because it may plug the pores of the catalyst and react with active phases. Alkali oxides and salts are major components in fly ash that could strongly decrease the oxidation activity of catalysts. Recently, studies have been made regarding the contribution of flue gas components, such as Cl_2, HCl, NOx, SO_2, NH_3 and H_2O for homogeneous Hg^0 oxidation [1,10]. Similar work has been performed to NOx removal by ammonia based on SCR catalysts. Kröcher et al. proposed that the deactivation of vanadium-based catalysts by alkali (earth) metals was exemplified in detail for K and Ca and the poisoning elements occupied the non-atomic hole sites of the V_2O_5 surface such that both the Brönsted acid and V–O sites are blocked [11,12]. This mechanism was able to quantitatively interpret the surface adsorption from a lab-scale study.

Therefore, we chose sodium (Na), potassium (K), magnesium (Mg) and calcium (Ca), four main alkali (earth) metal elements in main groups IA and IIA, respectively as the representative elements toward vanadium-based catalysts to investigate the deactivation

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Abbreviations: SCR, Selective Catalytic Reduction; BET, Brunauer, Emmett, and Teller equation; XRD, X-ray diffraction; TPD, temperature-programmed desorption; TPR, temperature-programmed reduction; XPS, X-ray photoelectron spectroscopy.

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performance and mechanism. This paper expands upon these initial efforts of trying to predict a course of deactivation performance and mechanism on mercury oxidation over vanadium-based catalysts. First, we elaborated upon the surface Hg^0 absorption by accounting for the major surface characteristics including BET surface area, XRD and Hg-TPD. Second, the redox ability was subjected to evaluations of fresh and alkali (earth) metal doped catalysts involving H_2-TPR and XPS analysis.

2. Materials and methods

2.1. Catalysts preparation

All of the catalysts in this work were prepared by wet impregnation method. The ammonium metavanadate (NH_4VO_3) and ammonium paratungstate [$(NH_4)_{10}(W_{12}O_{41})\cdot 5H_2O$] were mixed in the oxalic solution of desired proportions, and commercial TiO_2 (Degussa P25) was used as the precursor. $V_2O_5(1)$–$WO_3(9)/TiO_2$ catalysts, where numbers in brackets represent the mass percentage and are abbreviated as V1W9/Ti, were prepared by the dispersal of a certain mass of TiO_2 powder into 200 ml NH_4VO_3 and $(NH_4)_{10}(W_{12}O_{41})\cdot 5H_2O$ solution to obtain the slurry. The slurry was then stirred for 24 h, after that, heated to 110 °C for 12 h followed by calcinations at 500 °C for 4 h in air.

The doping process by alkali (earth) metals to V1W9/Ti (denoted as M*x*–V1W9/Ti, where *x* is the mass percentage of the alkali (earth) metal oxide, and M = Na, K, Mg or Ca) was prepared by different weights of Na_2O, K_2O, MgO and CaO thereby impregnating the prepared V1W9/Ti catalyst with aqueous solutions $NaNO_3$, KNO_3, $Mg(NO_3)_2$ or $Ca(NO_3)_2$, respectively. The alkali (earth) metals loaded catalysts were then stirred for 24 h, dried at 110 °C for 12 h and calcinated at 500 °C for 4 h. All the catalysts were ground and sieved to 40–60 mesh for activity evaluation.

2.2. Catalyst characterization

The prepared samples were characterized by BET surface area, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis. BET surface area, pore size and pore volume were measured by N_2 adsorption at 77 K using a Quantachrome AutoSorb AS-1 System. XRD measurements were carried out with a Rigaku D/max-2500 X-ray diffractometer using Ni filtered Cu Kα radiation. The applied current and voltage were 200 mA and 45 kV, respectively. During analysis, the samples were scanned from 10° to 90° at a speed of 6°/min. XPS data were obtained with a PHI Quantera SXM^{TM} (ULVAC-PHI Inc.). The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon.

Hg-TPD (Hg temperature-programmed desorption) was conducted by using a 0.2 g catalyst in a quartz reactor. The adsorption was performed by passing a gas mixture containing 200 $\mu g\,m^{-3}$ Hg^0 with N_2 as balance gas through the sample bed at 25 °C with the total flow rate of 500 ml/min. The experiment consisted of three stages: (1) sweep of the sample in N_2 at 500 °C for 2 h; (2) adsorption of Hg^0 for about 24 h until the adsorption gas was purged since mercury vapor was throughout and the concentrations were equal before/after the catalyst; (3) TPD measurements were carried out up to 500 °C at a heating rate of 10 °C/min with the total flow rate of 500 ml/min N_2. The concentration of Hg^0 was continuously recorded by an on-line Lumex RA 915+ Hg analyzer.

H_2-TPR (temperature-programmed reduction) experiments were conducted on a Micromeritics ChemiSorb 2720 using approximately 100 mg of samples. Samples were pretreated at 300 °C for 1 h in N_2 flow. The temperature was increased linearly from 50 to 1000 °C at 10 °C/min while H_2 consumption, with a concentration of 10%, was recorded continuously.

2.3. Activity measurement

Hg^0 conversion tests were obtained with an inlet gas stream of 500 ml min^{-1}. The basic composition of the inlet gas contained 80–100 $\mu g\,m^{-3}$ Hg^0, 8% O_2, 10 ppm HCl, and balanced with N_2. A stable concentration of Hg^0 was generated by a Dynacal Hg^0 permeation device (VICI Metronics) at a desired temperature. It would yield a stable Hg^0 concentration as long as the flow rate and water bath temperature were stable. Catalytic activity tests were performed in a U-shaped quartz tube reactor (760 mm in total length with an outer diameter of 8.0 mm and an inner diameter of 6.0 mm) held in a vertical position and surrounded by a large clam-shell furnace containing 200 mg of catalyst. The studies were carried out at different temperatures (100–500 °C). Hg^0 concentrations of influent and effluent were measured by switching the Hg analyzer both at the beginning and end of each test, based on which is capable to calculate Hg^0 conversion. The effects of H_2O and SO_2 on Hg^0 oxidation were tested by the addition of 8% (v/v) water vapor and 800 ppm SO_2. All the tubing was heated to a constant temperature of 120 °C to prevent the adsorption and condensation. For quality assurance and quality control (QA/QC), the instruments were calibrated before each test.

3. Results

3.1. Catalytic performance

3.1.1. Deactivation

Fig. 1a shows the Hg^0 conversion for fresh and alkali (earth) metal doped V1W9/Ti catalysts. As expected, the undoped V1W9/Ti catalyst showed the highest conversion at all temperatures with a maximum conversion of 95% and conversions in excess of 90% throughout the range of 200–400 °C. When alkali (earth) metals were doped, the deactivation performance caused by them seems to be similar, while the degree was differential. Actually, the measured conversion rate decreased from 95% without doping to 70% after doping at 300–400 °C, which might indicate some new chemicals formed or the structure was destroyed in the catalyst surface resulting in deactivations [13]. Another observation was that potassium caused the strongest reduction of Hg^0 conversion whereas the presence of magnesium in the V1W9/Ti catalyst showed the least deactivation effect: the decrease caused by Mg from 200 °C to 400 °C was quite substantial – two-thirds of that caused by Na and Ca. Meanwhile, deactivation effect caused by calcium was at the same level as sodium.

Fig. 1b shows the Hg^0 conversion over V1W9/Ti catalysts with different K doping amounts. It is clear that doping with 0.5% K_2O resulted in a slight deactivation; however, an increase of doping K_2O from 0.5% to 2% would lead to a more evident deactivation. Less than 65% Hg^0 conversion was observed for K2-V1W9/Ti even in the active temperature range. Based on these observations, the deactivation effect caused by all alkali (earth) metals can probably be ordered as follows: $K > Na \sim Ca > Mg$, and the deactivation performance increased proportionately with alkali (earth) metal doping amounts.

3.1.2. Effect of H_2O and SO_2

H_2O and SO_2 that exist unavoidably in flue gas have significant impacts on the catalytic activities. Here we present the effect of H_2O and SO_2 as shown in Fig. 2a and b. One of the basic findings by comparison with two figures is that V1W9/Ti catalyst had good resistance to H_2O (65–90% Hg^0 conversion), while K doped V1W9/Ti did not (20–60% Hg^0 conversion). When H_2O vapor was added into the gas stream over K doped V1W9/Ti in Fig. 2b, Hg^0 conversion declined 20–35%. It is an implication that the resistance capability

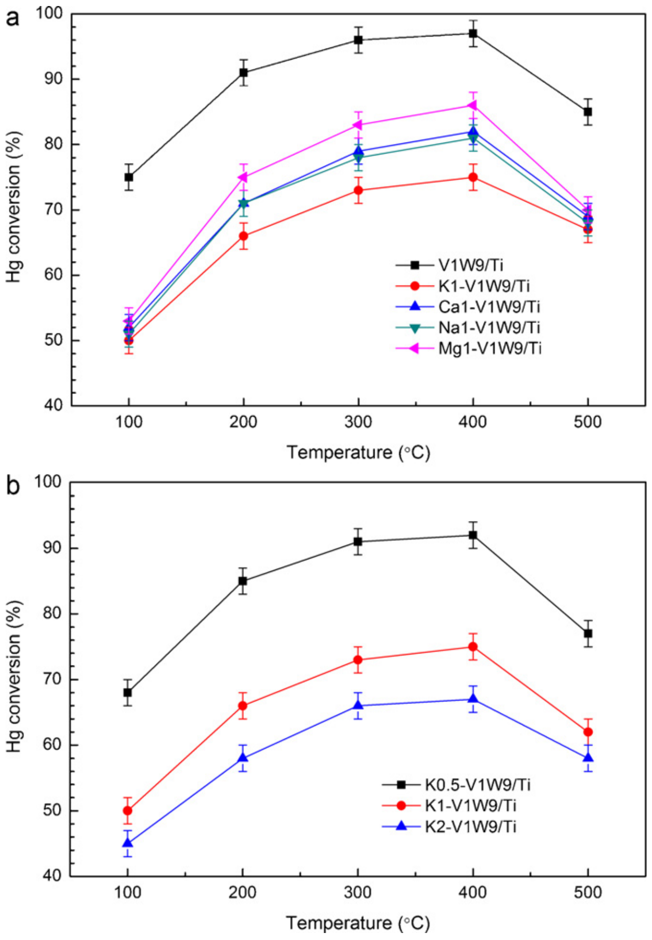

Fig. 1. Hg^0 conversion over V1W9/Ti, M*x*–V1W9/Ti (a) and different K loading doped V1W9/Ti (b) at different temperatures. Feed gas: Hg^0, HCl, O_2, N_2 as balance gas, GHSV = 100 000 h^{-1}.

to H_2O was not so good for K doped V1W9/Ti catalyst. The inhibition of H_2O at low temperature was obvious and could be explained mainly by the coverage of catalyst surface, while in high temperature range, the anti-water capability could be better based on the insubstantial competitive adsorption of water vapor with Hg^0.

In fact, the effect of SO_2 on Hg^0 conversion in flue gas was not conclusive, either promotional or inhibitory effects have been reported [14,15]. The addition of 800 ppm SO_2 had no obvious negative effects on Hg^0 conversion, and it seems to enhance Hg^0 conversion slightly in any temperature range while in dry condition. Furthermore, combined effects of H_2O and SO_2 were also studied. It is seen that the addition of H_2O and SO_2 could obviously enhance the catalytic activity, especially in a high temperature range. Thus, this promotional process may assume that the sulfate species were more easily formed and deposited on catalyst surface since SO_2 was introduced into the reaction, and the formed sulfate species could enhance the catalytic activation because of the newly formed sulfate adsorption acid sites [11].

3.2. Characterization

3.2.1. BET

The physical properties of V1W9/Ti and M*x*–V1W9/Ti catalysts including BET surface area, pore volume and pore diameters are summarized in Table 1. The BET surface area of V1W9/Ti was 48.9 m^2/g, the total pore volume was 0.386 cm^3/g, and the average pore diameter was 32.3 nm. Surface areas of M*x*–V1W9/Ti catalysts ranged from 40. 8 to 46.8 m^2/g, while a little lower than fresh V1W9/Ti. The similar circumstances that occurred to total pore volume seemed to illustrate that doping of alkali (earth) metals would cause the BET surface area and pore volume decrease somewhat. However, the average pore diameter did not show the same trend that could be associated with deactivations. Therefore, surface characteristics do not seem to be the dominant factor for the deactivation caused by alkali (earth) metals.

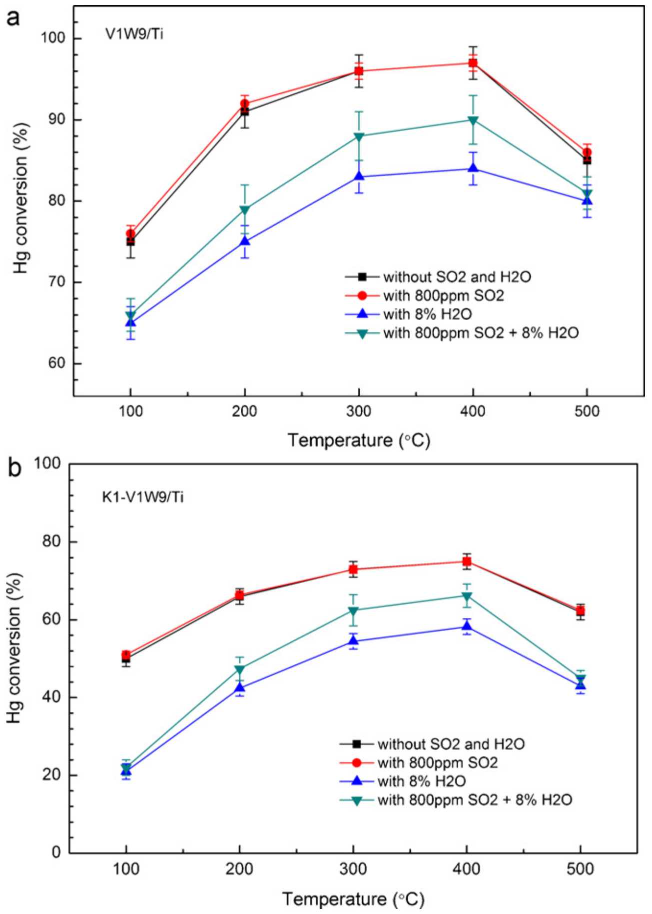

Fig. 2. Effect of SO_2 and H_2O on Hg conversion over (a) V1W9/Ti and (b) K1–V1W9/Ti. Feed gas: Hg^0, HCl, O_2, N_2 as balance gas, GHSV = 100 000 h^{-1}.

3.2.2. XRD

XRD patterns of V1W9/Ti and M*x*–V1W9/Ti were measured and are shown in Fig. 3, and the major features of XRD pattern belonged to TiO_2 including anatase phase together with a small amount of rutile phase. The active sites including V and W were barely detected because the crystallite sizes at low loadings are too small to be easily detected. As no obvious WO_3 phase was observed, it demonstrated that tungsten existed as a highly dispersed or amorphous surface species [16]. No peaks to alkali (earth) metal oxides were detected because the impregnations of alkali (earth) metals

Table 1
Physical properties of V1W9/Ti and alkali (earth) metals doped V1W9/Ti catalysts.

Samples	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
V1W9/Ti	48.9	0.386	32.3
Na1–V1W9/Ti	43.2	0.313	32.2
K0.5–V1W9/Ti	46.8	0.304	32.4
K1–V1W9/Ti	46.3	0.288	34.7
K2–V1W9/Ti	40.8	0.253	34.5
Mg1–V1W9/Ti	45.3	0.318	32.2
Ca1–V1W9/Ti	44.7	0.305	32.6

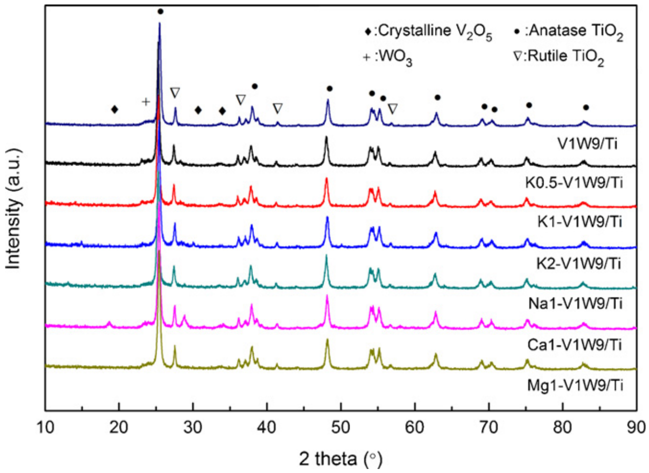

Fig. 3. XRD patterns of V1W9/Ti and M*x*–V1W9/Ti.

with the corresponding oxides were low on the surface, which subsequently does not change the basic XRD patterns. It is ascertained that supporting vanadium oxides on anatase TiO_2 leads to very strong oxidation activities [17], more active than those obtained by doping of alkali (earth) metals. It is interesting to point out that there were two vanadium peaks showing in Ca and Mg doped catalysts rather than in K and Na doped catalysts as evidenced by the absence of diffraction peaks at $2\theta = 18.60$ and $2\theta = 34.04$. That could be explained that K and Na have good dispersion on the catalyst surface compared to Ca and Mg, which prevented vanadium from being well distributed on the surface, and thus caused deactivations. While the content of K increased from 0.5% to 2%, the peak of V_2O_5 crystallites became weaker and less obvious; this means that the active component of vanadium might be covered by K [18]. As discussed above, the doping process caused the possible decrease of surface area and total pore volume. Since no visible crystalline of alkali (earth) metals were observed, it may be concluded that the activated sites of vanadium were influenced and even decreased by doping alkali (earth) metals.

3.2.3. *Hg-TPD*

It has been established that surface adsorption played an important role in the surface oxidation of Hg^0. One of the most important steps for oxidation is Hg^0 adsorption in the catalyst surface [2,13]. Hence, Hg-TPD experiments were carried out to investigate the deactivation performance caused by alkali (earth) metals. Fig. 4 shows the Hg-TPD curves and Table 2 gives the detailed information of V1W9/Ti, Na1–V1W9/Ti, K1–V1W9/Ti, Mg1–V1W9/Ti and Ca1–V1W9/Ti catalysts, which were obtained in the temperature range of 30–500 °C. All curves exhibited two Hg^0 desorption peaks around 180 °C and 260 °C which corresponded to weakly bound and strongly bound Hg species, respectively [16].

It is important to note that Hg^0 desorption peak over K1–V1W9/Ti was much lower than on any other catalysts. In low temperature range, Hg^0 desorption peak on Ca1–V1W9/Ti and Mg1–V1W9/Ti was higher than V1W9/Ti; while in high temperature range, the Hg^0 desorption peak of strongly bound Hg^0 species was highly weakened on M*x*–V1W9/Ti. For K1–V1W9/Ti and Na1–V1W9/Ti, Hg^0 desorption peak also showed a trend in which high temperature surface adsorption capability was neutralized much more heavily. Thus, the orders for the Hg^0 desorption amount in low and high temperature ranges were: (1) Mg1–V1W9/Ti, Ca1–V1W9/Ti, V1W9/Ti ∼ Na1–V1W9/Ti, K1–V1W9/Ti; (2) V1W9/Ti, Mg1–V1W9/Ti, Ca1–V1W9/Ti ∼ Na1–V1W9/Ti, K1–V1W9/Ti. However, it is expected that total Hg^0 desorption amount was calculated as about 59.6 (fresh), 52.8 (Mg), 26.1 (Ca), 19.7 (Na) and 8.3 (K) μmol/g. Therefore, Hg^0 desorption amounts in fresh and alkali (earth) metal contained catalysts increase as: K1–V1W9/Ti, Na1–V1W9/Ti, Ca1–V1W9/Ti, Mg1–V1W9/Ti and V1W9/Ti. This could be explained by the acid sites variations caused by alkali (earth) metals since it was reported [8] that Hg^0 could be adsorbed at different acid sites or some kinds of coverage in the surface active sites. Consequently, Hg-TPD results were well associated with Hg^0 conversion trend and alkalinity value, which indicated that alkali (earth) metals would decrease surface Hg^0 adsorption. Hence, Hg^0 absorption in catalyst surface seems to be the first important step for the following reactions.

3.3. *Redox ability*

3.3.1. *H_2-TPR*

The redox ability of vanadium and tungsten species is considered as another key factor in SCR reaction [19,20]. Thus, the effects of alkali (earth) metals on the reducibility behavior toward vanadium and tungsten species were investigated with H_2-TPR profiles as shown in Fig. 5. It is obvious that two main reduction peaks appeared in all the curves. The peaks of V1W9/Ti appeared around 500 °C and 800 °C, corresponding to the reduction of V^{5+}–V^{3+} and W^{6+}–W^0, respectively [21,22]. In comparison, when alkali (earth) metals were doped into V1W9/Ti, the reduction peaks of V and W species showed different changes. In the case of Na1–V1W9/Ti, K1–V1W9/Ti, Mg1–V1W9/Ti and Ca1–V1W9/Ti,

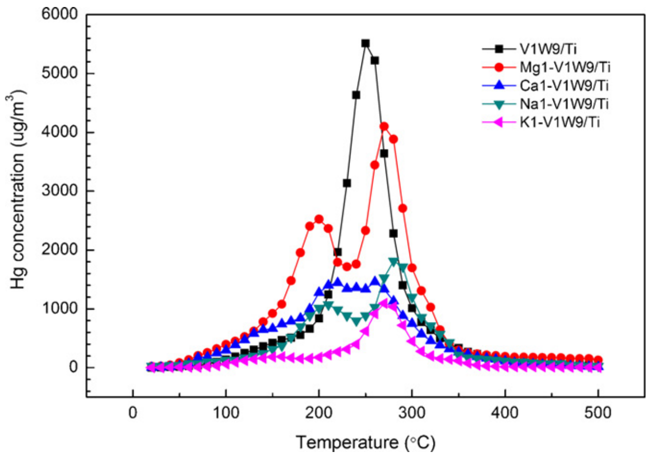

Fig. 4. Hg-TPD profiles of V1W9/Ti and M*x*–V1W9/Ti.

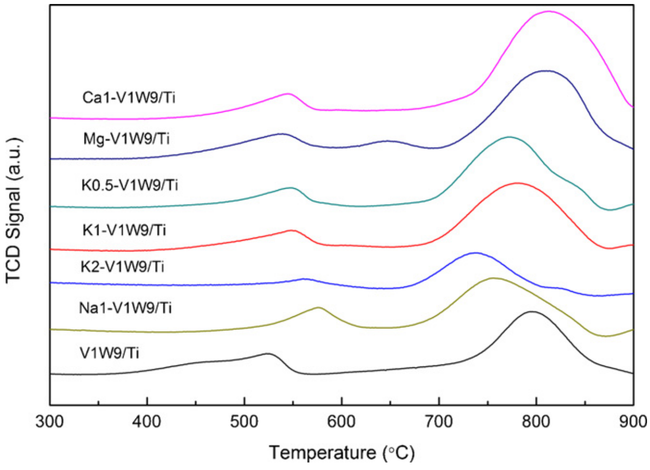

Fig. 5. H_2-TPR profiles of V1W9/Ti and M*x*–V1W9/Ti.

Table 2
Hg-TPD information of V1W9/Ti and alkali (earth) metals doped V1W9/Ti catalysts.

Samples	Fitting peak number	Peaking temperature (°C)	Peak area	Desorption amount (μmol/g)	Alkalinity value[a]
V1W9/Ti	2	150, 250	395,305.9	59.6	–
Na1–V1W9/Ti	2	210, 280	211,857.1	19.7	~14.1
K1–V1W9/Ti	2	170, 270	89,328.5	8.3	~14.3
Mg1–V1W9/Ti	2	200, 270	363,821.4	52.8	10.4
Ca1–V1W9/Ti	2	220, 260	241,528.5	26.1	11.7

[a] pH value of MxO saturated water solution.

the reduction peaks of V species shifted to higher temperatures, while the peaks of W species shifted to lower temperatures. For K1–V1W9/Ti with different K loadings, the reduction peaks of V species showed apparently the same trend as higher temperatures with the increasing loadings. All the results indicated that doping alkali (earth) metals into vanadium-based catalysts could decrease the reduction of vanadium species. It is hard to separate the effect caused by certain elements in the same main group according to TPR profiles, but the difference between the elements in groups IA and IIA was quite distinct. The drop of the vanadium reducibility in Na1–V1W9/Ti and K1–V1W9/Ti was much more drastic than that in Mg1–V1W9/Ti and Ca1–V1W9/Ti, which could be correlated to the observed Hg^0 deactivation performance. It is assumed that Na and K are more active and can influence the chemical environment around W species more drastically than Mg and Ca, which caused the obvious peak variation of V species. In addition, W species on vanadium–titanium catalysts are generally known to improve SCR reaction on the surface [6,23]. Therefore, the promoting effects caused by W species for Hg^0 oxidation may also exist mainly according to the enhancement of the vanadium reducibility, since the increase of surface adsorption and induction of the formation of polymeric vanadate on the catalyst surface have been reported [16]. However, the interaction between alkali (earth) metals and W species cannot be observed and well associated with deactivations.

3.3.2. XPS of O 1s

Granite et al. [24] studied various metal oxides for Hg^0 catalytic oxidation and proposed that lattice oxygen of the metal oxides could serve as an oxidant, forming mercuric oxide (HgO). It has also been reported that lattice oxygen was the most abundant reactive intermediates that were responsible for oxidative dehydrogenation of alkanes over vanadium-based catalysts [25]. Gas-phase O_2, on the other hand, re-oxidizes the reduced metal oxides, replenishing the lattice oxygen [24,25]. Combined with the above results, the addition of alkali (earth) metals could influence the surface reducibility of vanadium and tungsten species, such as surface oxygen. It is also reported that surface chemisorbed oxygen is a kind of most active oxygen and plays an important role in oxidation reactions [26], and the relatively high concentration ratio of $O\alpha/(O\alpha+O\beta)$ on catalyst surface could be correlated with high oxidation activity [27]. Therefore, XPS analysis of O 1s in fresh and alkali (earth) metals doped samples was performed as shown in Fig. 6, while surface atomic concentration results are displayed in Table 3. It is clear that the O 1s peaks could be fitted into two peaks referred to lattice oxygen at 529.3–530.0 eV (hereafter, denoted as Oβ) and chemisorbed oxygen belonging to the defect-oxide or the hydroxyl-like group at 531.3–531.9 eV (hereafter, denoted as Oα) [21]. After doping alkali (earth) metals onto V1W9/Ti, the $O\alpha/(O\alpha+O\beta)$ ratio decreased, especially for Na and K. The content order of the $O\alpha/(O\alpha+O\beta)$ ratio was calculated as: V1W9/Ti (26%), Mg1–V1W9/Ti (25%), Ca1–V1W9/Ti (17%), Na1–V1W9/Ti (14%) and K1–V1W9/Ti (12%), and this trend was again in good agreement with Hg^0 deactivation performance. Therefore, the observed variations of O 1s signal after doping alkali (earth) metals could be explained by the formation of strong bounds between surface oxygen centers and the metal-dopant, and then the reducibility of surface species decreased based on TPR results. This might indicate that the low concentration of surface chemisorbed oxygen leads to the deactivation performance. Additionally, doped alkali (earth) metal oxide with stronger alkalinity value could occupy the surface oxygen vacancy more firmly, then reducing the chemisorbed oxygen and activity of vanadium species. Consequently, the decrease of Hg^0 adsorption, surface chemisorbed oxygen and surface vanadium species could be the main reasons why vanadium-based catalysts were poisoned by alkali (earth) metals.

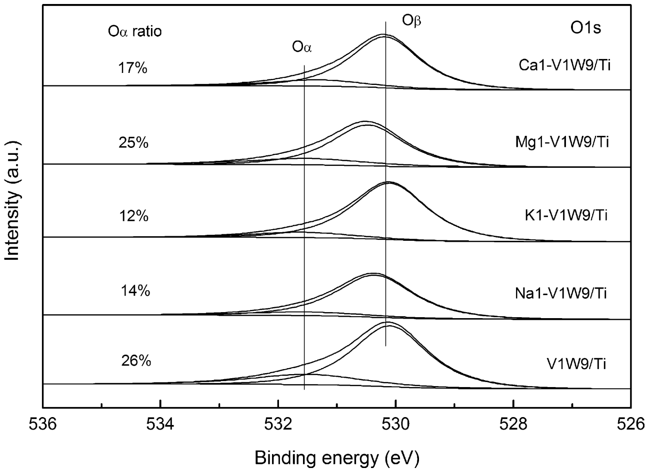

Fig. 6. XPS results of O 1s in V1W9/Ti and M*x*–V1W9/Ti.

Table 3
XPS results of V1W9/Ti and alkali (earth) metals doped V1W9/Ti catalysts.

Samples	Surface atomic concentration (%)				
	V	M	W	O	Ti
V1W9/Ti	1.45	–	4.49	70.62	23.44
Na1–V1W9/Ti	–	0.89	4.34	72.36	22.41
K0.5–V1W9/Ti	–	1.21	4.29	72.36	22.14
K1–V1W9/Ti	–	2.06	4.21	70.23	23.50
K2–V1W9/Ti	–	4.13	4.04	69.43	22.4
Mg1–V1W9/Ti	–	1.17	4.10	73.78	20.95
Ca1–V1W9/Ti	–	1.13	4.38	73.11	21.38

4. Discussion

On the basis of the above results, it may be concluded that Hg^0 oxidation states were deactivated by alkali (earth) metals and the deactivation performance of K, Na, Ca and Mg was increased as alkalinity value. Results of BET surface area and XRD showed that no obvious structural change occurred, both of which contributed little toward the deactivations. However, surface Hg^0 adsorption and redox ability (Oα) could be the main influential factors.

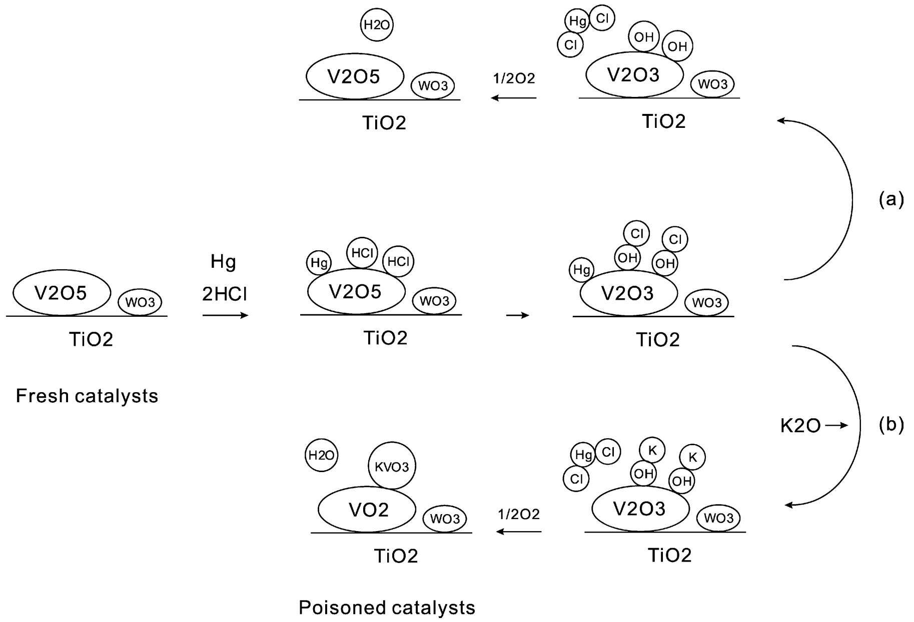

Fig. 7. Poisoning mechanism of K doped V1W9/Ti on Hg^0 oxidation.

It is reported that chlorine and surface Oα have strong affinity for metal oxides, and HCl participates in Hg oxidation reacted with surface activated vanadium generating (OH)Cl group [8,28], so vanadium oxychloride complexes such as $V_2O_3(OH)_2Cl_2$ are expected to be formed by the reactions between gaseous HCl and surface O over vanadium-based catalyst. Actually, the $V_2O_3(OH)_2$ structures are also one type of the active sites readily present on the surface [5]. Thus, $V_2O_3(OH)_2Cl_2$ and $V_2O_3(OH)_2$ species can react with adsorbed Hg^0 to generate an intermediate HgCl and (OH)Cl–Hg species, which then further reacts with chlorine species to form a more stable mercuric chloride, $HgCl_2$. The catalytic process could consist of four simplified steps and predict as: (1) Hg^0 and HCl adsorption on catalyst surface; (2) decomposition of HCl by the surface O to form $V_2O_3(OH)_2Cl_2$ species; (3) complexation of Hg^0 by activated $V_2O_3(OH)_2Cl_2$ to generate $V_2O_3(OH)_2$ and an intermediate HgCl species, which then further reacts with chlorine species to form a more stable mercuric chloride, $HgCl_2$; (4) oxidation of $V_2O_3(OH)_2$ by gas-phase O_2 to form V_2O_5 [5,8,28].

However, the deactivation process and mechanism would be somewhat different from the oxidation process. One basic statement is that HCl may not react with alkali (earth) metals to form stable salts but preferring to integrate with vanadium-based catalysts. Research [19] reported that the strength and number of Brönsted acid sites could be decreased with the loading of alkali (earth) metals. With the increasing K amount, the position of the band due to V=O stretching slightly shifts to a lower wave number, and possibly splits, suggesting that K_2O modified the surface vanadium intermediate species. Additionally, the band due to the O=V–OH groups decreased in intensity upon higher amounts of K_2O addition, and the formation of O=V–OHCl would also be replaced by doping alkali (earth) metals. It is an implication that potassium added to the catalyst migrated toward the O=V–OH and/or O=V–OCl groups preferentially. Therefore, the activated vanadium would change to inactive metavanadate species in the catalyst surface, resulting in significant deactivations; even trace amount of K_2O would also make a substantial decline in activity, indicating the combination priority of K_2O with the Brönsted acid sites in the vanadium catalyst [19]. On the basis of experimental data and the surface analysis in this study, one poisoning mechanism of Hg^0 oxidation process over the vanadium-based catalyst was proposed and shown in Fig. 7. The quantity of Brönsted acid sites was decreased when doping alkali (earth) metals, and the formation of $V_2O_3(OH)_2Cl_2$ could be inhibited by the formation of inactive metavanadate species, such as KVO_3 in path (b). Consequently, the formation of inactive metavanadate species could be responsible for the deactivation performance caused by alkali (earth) metals over vanadium-based catalyst for oxidation of gaseous elemental mercury.

5. Conclusions

Na, K, Mg and Ca were chosen as representative alkali (earth) metals to investigate the deactivation performance over V_2O_5–WO_3/TiO_2 catalysts on mercury oxidation in simulated flue gas. Deactivation performances of Hg^0 conversion over alkali (earth) metals doped catalysts were associated with alkalinity value and ordered as: K > Na ∼ Ca > Mg. BET and XRD results showed that no obvious structure change occurred. Surface adsorption and redox capability could thus be the main responsible factors. Results demonstrated that surface characteristics were not the determinants of Hg^0 oxidation activity or the deactivation. The surface coverage by alkali (earth) metals possibly caused decrease in the surface area and total pore volume. Hg-TPD results indicated that the doping of alkali (earth) metals would decrease surface Hg^0 adsorption. Low concentration of surface chemisorbed oxygen could lead to the deactivation performance according to the H_2-TPR and XPS of O 1s results. Consequently, the decrease of Hg^0 adsorption and surface redox ability (Oα), and the formation of inactive metavanadate species, such as KVO_3 could be responsible for the deactivation performance caused by alkali (earth) metals over vanadium-based catalyst for oxidation of gaseous elemental mercury.

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