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Design of dual functional adsorbent/catalyst system for the control of VOC's by using metal-loaded hydrophobic Y-zeolites

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Abstract

To design a good combined adsorbent/catalyst dual functional system for the control of the low concentration VOC, both adsorption and catalytic activity test over metal-loaded zeolite HY were carried out. Hydrophobic HY zeolite was selected as a good adsorbent candidate among the tested zeolite adsorbents and extended to the catalyst support material by adding various transition metals. The temperature programmed surface reaction (TPSR) of toluene and methylethylketone (MEK) suggested the silver as the best candidate among the tested transition metals. Temperature programmed reductions (TPR) and O_2-temperature programmed desorption (O_2-TPD) on Ag/HY catalysts were carried out to explain the nature of active centre of Ag catalyst for the toluene oxidation. Silver oxide species or partially oxidized metallic silver on to the surface of metallic silver phase was proposed as an active redox site during the oxidation reaction.

Keywords: VOC; Ag loaded zeolite HY; Adsorption; Catalytic oxidation; Hydrophobic molecular sieve (HMS); Dual functional adsorbent/catalyst

1. Introduction

Volatile organic compound (VOC) is considered as one of the main air pollutants, and in many countries, legislation has already been introduced to reduce their emission. Besides main emission sources such as petroleum industries, there are a lot of local sources such as painting, printing and laundry which emit VOC stream of low concentration. While catalytic oxidation can be considered to be an effective way for complete destruction of VOC, it is not economically feasible for the low concentration VOC. Among various control technologies for lean VOC stream, the advanced adsorption process is the most promising [1–3]. The advanced adsorption process is composed of adsorption unit followed by catalytic incinerator or condenser for recovering valuable solvents. Combined with energy saving adsorption process, catalytic oxidation can be even more effective for the control of low concentration VOC. Moreover, the concept of advanced adsorption can be further extended by the dual functional adsorbent/catalyst system, which integrates the adsorption and catalytic incineration into a single control unit [1].

The use of hydrophobic zeolite for the dual function adsorbent/catalyst medium is justified in two aspects. One is safety concern for the operation of catalytic oxidation at high temperature, and another is high adsorption affinity for VOC in humid condition. Activated carbons are generally used in many adsorption processes because of their higher adsorption capacity and good economy. However their regeneration is very difficult because of their thermal and chemical instability causing significant safety problems. Since Blocki [2] proposed hydrophobic zeolite as a promising adsorbent, which is superior to activated carbon due to their resistance to humidity and their non-flammability, the use of hydrophobic molecular sieves (HMS) such as high silica zeolites is emerging for the adsorption of VOC's [4].

Selection of effective and economical catalyst components is as important as the selection of good adsorbent materials to embody the best dual functional adsorbent/catalyst media. Noble metal-based catalysts such as supported platinum and palladium are traditional catalysts for the low temperature complete oxidation [5–7]. However those catalysts, although very active for oxidation, are too expensive and susceptible to poisoning by chlorine/chloride products [8].

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Mixed metal oxides of group VB–IB are generally used for oxidation of CVOCs. Silver has been well known for its epoxidation activity [9] and recently gained much interest on SCR of NO by hydrocarbons [10–13] and the deep oxidation of CO and methane [14,15]. However there are few reports for their application to the complete oxidation of VOC's [16–19].

In this study, zeolites of different structure were tested for the adsorption of VOC (toluene as a model compound) by means of dynamic adsorption experiment and selected zeolite adsorbent (HY) was used as support material for VOC oxidation catalysts to develop dual functional adsorbent catalyst medium. Various transition metals (Mn, Fe, Co, Ni, Cu, Zn, Ag) were tested for the catalytic oxidation of toluene and methylethylketone (MEK) and silver was found as a good candidate. Catalytic properties of selected Ag/HY dual functional media were further investigated in terms of the relationship between the catalytic activity and the nature of active sites.

2. Experimental

2.1. Materials

Commercial zeolites of different pore structures were purchased from Zeolyst Co. (Table 1). To endow the catalytic activity, series of transition metals (Fe, Co, Ni, Cu, Zn, Ag) and precious metals (Pt, Pd) were introduced into the zeolite HY using nitrate precursor of each metal. Excess water impregnation method was applied to incorporate metallic components within the zeolite HY. The silver loaded HY (Ag(*x*)/HY, *x*: weight percent of Ag) catalyst was prepared for the improvement of catalytic activity of dual functional system. For the preparation of the silver ion-exchanged HY ($x = 0.5$), 25 g of HY and 2 L of $AgNO_3$ solution (0.005 M) were stirred at room temperature for 1 day. The ion exchange was repeated three times to achieve high silver loading ($x = 2.4$). All the above procedures were performed in the dark due to the sensitivity of silver to light. The silver content in ion-exchanged sample was analysed by inductively coupled plasma emission spectrometry (ICP). To reach higher loading beyond the ion-exchange capacity of zeolite, further impregnation was carried out by excess water impregnation method. All catalysts were calcined at 500 °C for 3 h in air flow condition. Detailed preparation method and physical properties are summarized in Table 2.

Table 1
Physical and chemical properties of selected adsorbents

Name	Structure	Si/Al_2	Surface area (m^2/g)	Pore volume (cm^3/g)
HY(80)	FAU	80	681	0.47
HMOR	MOR	90	553	0.33
HZSM-5	MFI	280	393	0.24
H-Beta	BEA	300	661	0.39
A.C.[a]	n.a.[b]	n.a.[b]	936	0.73

Zeolites from Zeolyst Co.

[a] Activated carbon from Aldrich Co.

[b] Not applicable.

2.2. Adsorption and desorption

Adsorption and desorption of toluene were carried out in a microflow adsorption bed followed by quadrupole mass spectrometer for the effluent gas analysis. Breakthrough curves for each of 0.05 g adsorbent were acquired at room temperature and the adsorption capacities could be determined by calculating the areas from breakthrough curves. Inlet stream for dynamic adsorption was a mixture of 1000 ppm toluene in air carrier with a flow rate of 20 STP cm^3/min. After reaching the adsorption saturation, temperature programmed desorption (TPD) curves were obtained to follow the desorption dynamics of each adsorbent. Helium flow at a rate of 20 STP cm^3/min was used for the desorption of adsorbed toluene, and the heating rate of adsorbent was 5 °C/min.

2.3. Catalytic activity test

Temperature programmed surface reaction (TPSR) was carried out to compare the catalytic activity for every 0.05 g of metal-loaded HY (M/HY) catalyst. Before raising temperature, catalyst was pre-treated at 400 °C for 2 h in He flow, cooled to room temperature and fully saturated with VOCs by flowing reactant stream (1000 ppm toluene or MEK in air). Catalyst bed temperature was raised at a rate of 5 °C/min and the flow rate of the reactant stream was fixed at a space velocity of 6000 h^{-1}. VOC concentration of effluent stream was continuously monitored using quadrupole mass spectrometer.

Catalytic oxidation of toluene over selected Ag/HY catalyst was carried out in a fixed bed reactor (11 mm i.d. and 500 mm length) for detailed reaction studies. A 0.1 g of Ag/HY catalyst was loaded in a quartz reactor and the space velocity was 15 000 h^{-1}. Toluene conversion was determined after 1 h reaction at each temperature using online HP6890 gas chromatography (GC) with flame ionization detector (FID), and CO/CO_2 selectivity was analysed by GC-FID system equipped with methanizer.

2.4. Characterization

The surface areas and pore volumes were measured by the nitrogen adsorption method (Micromeritics ASAP2000). The structures of zeolites and metallic component of dual functional media were confirmed by their powder X-ray diffraction (XRD) patterns using Rigaku X-ray analyzer with Cu Kα radiation.

Temperature programmed reduction (TPR) and temperature programmed desorption (TPD) were carried out in a conventional flow apparatus with a thermal conductivity

Table 2
Preparation methods and physical properties of catalysts

Catalyst	Silver loading (wt.%)	Preparation method	Surface area (m^2/g)		Pore volume (cm^3/g)	
			Fresh	After reaction[a]	Fresh	After reaction[a]
Ag(0.5)/HY	0.52	One time IE	678	678	0.48	0.48
Ag(2.4)/HY	2.40	Three times IE	690	667	0.49	0.46
Ag(1)/HY	1.00	Impregnation	663	663	0.46	0.46
Ag(3.4)/HY	3.40	Three times IE—impregnation	670	666	0.47	0.47
Ag(5)/HY	5.00	Impregnation	633	624	0.44	0.45
Ag(7.4)/HY	7.40	Three times IE—impregnation	592	580	0.44	0.43
Ag(10)/HY	10.00	Impregnation	558	544	0.41	0.40
Ag(12.4)/HY	12.40	Three times IE—impregnation	511	509	0.40	0.40
Ag(20)/HY	20.00	Impregnation	423	429	0.35	0.35
Ag(22.4)/HY	22.40	Three times IE—impregnation	322	320	0.31	0.31

IE: ion-exchange.

[a] After reaction at 400 °C for 1 h.

detector (TCD). For TPR study, the 4 A molecular sieve trap was used to eliminate the produced H_2O during reduction. A 0.1 g sample was pre-treated in air at 500 °C for 1 h, cooled to room temperature and exposed to a flow of H_2 (5 vol.%)/Ar mixture. The temperature was programmed with a constant heating rate of 10 °C/min.

For O_2-TPD, a 0.1 g of sample was pre-treated in air at 500 °C for 1 h and then cooled to room temperature. After the sample was kept in helium flow of 30 STP cm^3/min for 30 min, the temperature of the sample was raised at a constant rate of 10 °C/min and the amount of desorbed oxygen was monitored by a TCD detector.

3. Results and discussion

3.1. *Dynamic adsorption and temperature programmed desorption of toluene*

Fig. 1 shows the toluene adsorption breakthrough curves of selected adsorbents. Among the zeolite adsorbents tested, hydrophobic zeolite HY (SiO_2/Al_2O_3 = 80) showed the largest adsorption capacity. Although the total adsorption capacity is smaller than activated carbon, the breakthrough time of HY exceeded that of the activated carbon. As shown in Fig. 1, the time for exceeding the outlet concentration of toluene (95% removal or C/Co = 0.05) is a measure of adsorption performance for inlet stream of lean VOC. As shown in Table 1, HY has the highest surface area and pore volume, resulted in the highest adsorption amount. Results in N_2 adsorption is quite well matched with dynamic adsorption tendency in Fig. 1.

Fig. 2 shows the results of temperature programmed desorption of adsorbed toluene. Zeolite adsorbents generally show lower desorption temperature and narrower desorption temperature window than activated carbon. HY showed its desorption peak at a lowest temperature below 100 °C, which might come from its large pore opening and the existence of supercage in its pore structures.

Therefore, HY was suggested as the best adsorbent for the application to the dual functional adsorbent/catalyst medium. Its large adsorption capacity comparable to activated carbon and its unique desorption dynamics, i.e., low and narrow desorption temperature window must be suit-

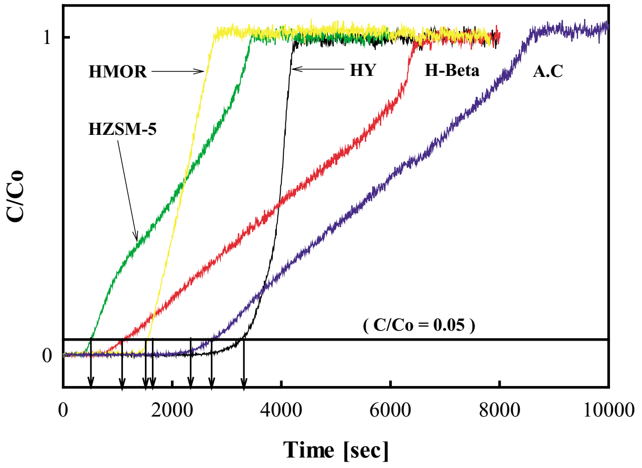

Fig. 1. Adsorption breakthrough curves of toluene over selected zeolite adsorbents.

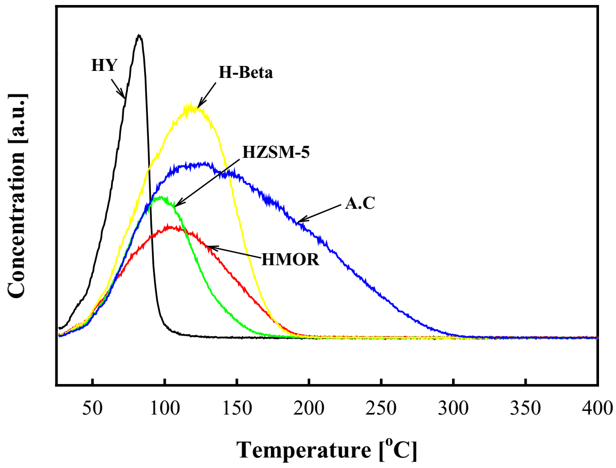

Fig. 2. Temperature programmed desorption of toluene over selected zeolite adsorbents.

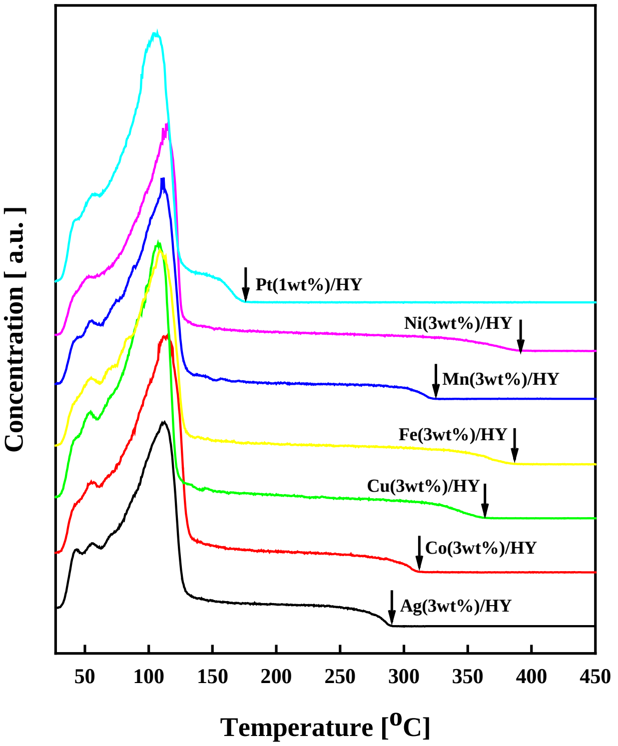

Fig. 3. Temperature programmed toluene oxidation reaction over M/HY catalysts.

able for designing the continuous adsorption-regeneration cycling system.

3.2. *Catalytic oxidation—the screening of primary component*

Catalytic activity was endowed to selected HY zeolite adsorbent/catalyst support by incorporating active metal compounds. Fig. 3 shows the TPSR results of different metal-loaded HY catalysts. Space velocity for screening test was fixed on 6000 h^{-1}. First peak around 100 °C corresponds to the amount of desorbed toluene which was adsorbed before TPSR started. The temperature for surface reaction was increased after full saturation was achieved. After complete desorption of pre-adsorbed toluene, conversion due to catalytic function, indicated as an arrow, started at around 150 °C for noble metals and 300–400 °C for transition metals, respectively. Except noble metals, which are too expensive and vulnerable to poisonous impurities, Ag/HY showed the best activity on the VOC oxidation reaction. The temperature of toluene desorption over Ag/HY catalyst was around 290 °C while those of other transition metal impregnated Y were above 350 °C. The activities of M/HY catalysts on the toluene and methylethylketone (MEK) were summarized in terms of complete conversion temperature (T_{100}) in Table 3. Ag/HY catalyst showed the lowest conversion temperature for both toluene and MEK oxidation. Catalytic activity was enhanced as their silver loading increased.

Table 3
Activity (T_{100}) of M/HY catalyst on VOC oxidation by TPSR

Catalyst M(x)/HY(80)		T_{100}	
M	x	Toluene oxidation	MEK oxidation
Ag	1	330	310
Ag	3	290	260
Mn	1	385	305
Mn	3	320	273
Fe	1	415	340
Fe	3	390	316
Co	1	350	325
Co	3	310	297
Cr	1	385	330
Cr	3	360	321
Cu	1	355	290
Cu	3	360	274
Ni	1	420	360
Ni	3	395	352
Pt	1	175	210
Pd	1	170	200

Reaction condition: 1 atm, SV = 6000 h^{-1}.

3.3. *Characterization of Ag/HY catalyst*

The successful design of effective dual functional adsorbent/catalyst medium can be achieved through optimising the catalyst properties. In this regard, it is desirable to investigate the nature of active sites on the Ag/HY catalyst. Fig. 4 shows the activities of Ag(x)/HY catalysts on the toluene oxidation. Ion-exchanged catalysts ($x = 0.5, 2.4$) and lower loading catalysts ($x = 1, 3.4$) showed quite low activity compared to higher loading catalysts ($x \geq 5$) and it can be seen that the activity increased with silver loading.

Figs. 5 and 6 show the XRD patterns and TPR curves of Ag(x)/HY catalysts, respectively. From the XRD peaks on $2\theta = 38.1$ and 44.3, it is clear that the metallic Ag phase is formed at a high loading of Ag, i.e., $x \geq 5$. And its intensity gradually increased as the Ag loading increased. These interesting patterns with increased Ag loading are also observed in TPR curves of Fig. 6 and also in O_2-TPD curves of Fig. 7. In TPR curves of Fig. 6, Ag(x)/HY catalyst showed gradual increase of peak around 100 °C, and O_2 liberation peak around 480 °C in Fig. 7 and the toluene conversion in Fig. 4 showed the same pattern with silver loading.

From these results, it might be assumed that the metallic Ag could play an important role in the oxidation of toluene at any rate. Kundakovic and Flytzani-Stephanopoulos [15] claimed that the formation of large polycrystalline Ag particles is favoured at high Ag loading on zirconia support and that partially oxidized metallic Ag state in the oxygen condition could be the active phase for the methane deep oxidation. They also have pointed out that the Ag^+ isolated ions in acidic zeolite supports had poor methane oxidation activity. In our experiments, ion-exchanged catalyst showed poor activities as shown in Fig. 4, and its main Ag state might be the isolated Ag^+ or well dispersed Ag_2O within zeolite's

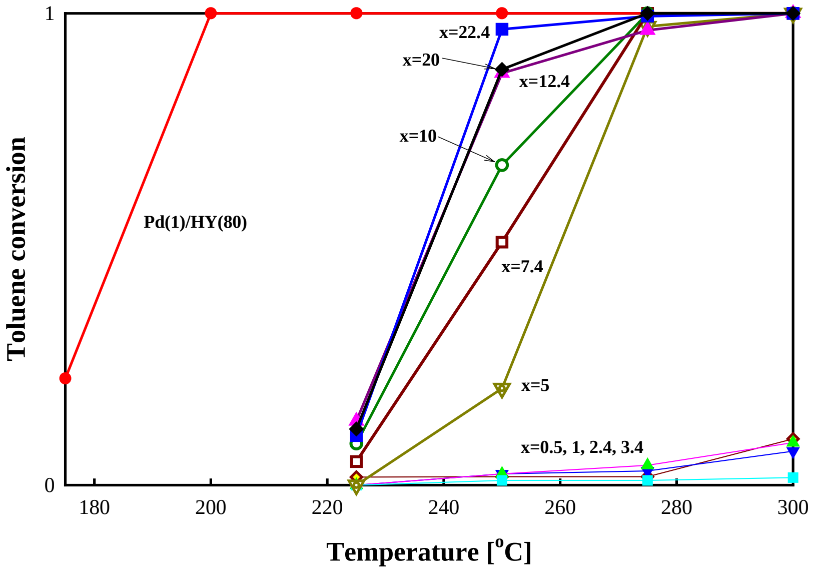

Fig. 4. Activity of toluene oxidation over Ag(x)/HY catalyst in a fixed bed reactor (SV = 15 000 h^{-1}).

micropores. However as the loadings of Ag increased, the portion of metallic Ag phase increased coincidently with the oxidation activity as shown in Figs. 5 and 4, respectively. It was observed with transmission electron microscopy (TEM) that the number of Ag particles (10–20 nm in size) on zeolite surface increased with the loadings. These Ag nanoparticles must contribute to the high toluene oxidation activity.

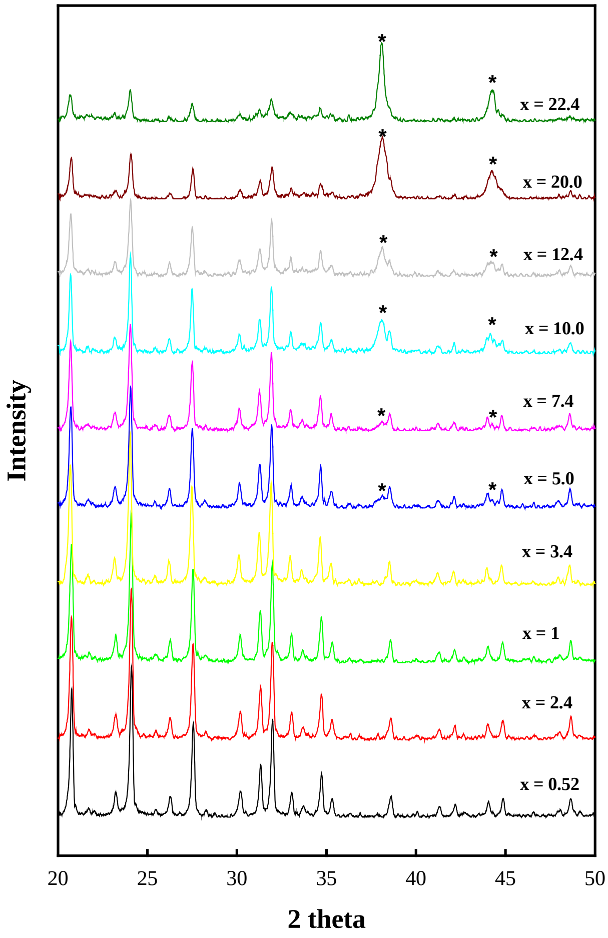

Fig. 5. XRD of Ag(x)/HY catalyst ('*' is for the metallic silver phase).

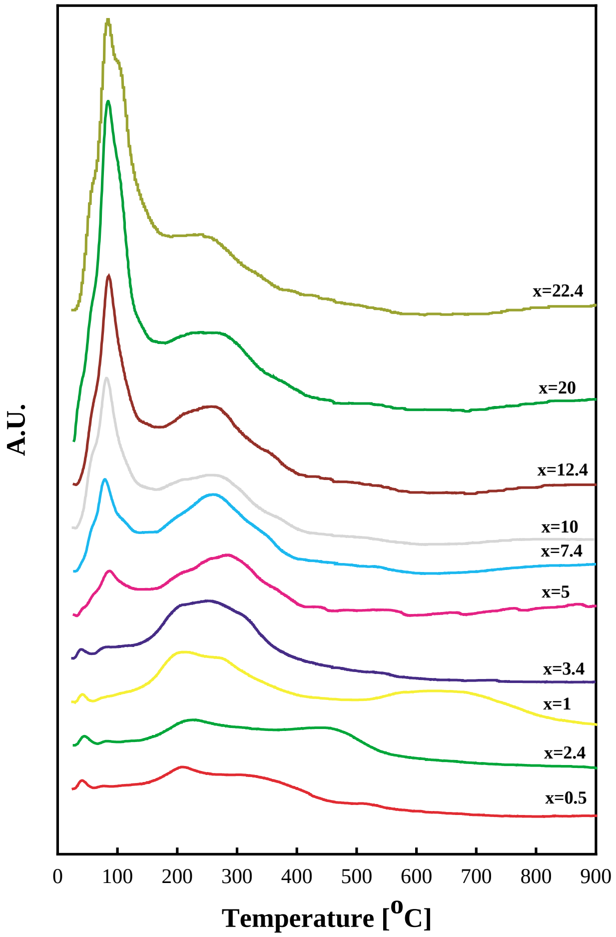

Fig. 6. H_2-TPR of Ag(x)/HY catalyst.

The TPR curves in Fig. 6 shows three distinct groups of peaks, low temperature peaks around 100 °C, mid-temperature peak between 200 and 300 °C and broad peak in high temperature region. Even though the bulk AgO and Ag_2O reduction peak was reported to appear at around 100 and 140 °C, respectively [11], the low temperature peak around 100 °C in the present study should not be assigned as the bulk silver oxide peak. In our experiments, the air pre-treatment for 1 h at 500 °C was carried out before TPR measurement in order to make the same condition as the oxidation reaction. It should be reminded that the bulk silver oxides decompose to metallic Ag rapidly at a temperature of 250 °C in air [13,20] and that the present work, together with Luo et al.'s [18] confirm the decomposition of Ag_2O at 400 °C under helium flow as shown in Fig. 7. Bethke and Kung [13] reported that three main peaks (129, 275, 648 °C) were observed for 4 wt.% Ag-ZSM-5 which is highly acidic support ($Si/Al = 19$) during TPR after O_2 treatment for 1 h at 500 °C. They suggested that the peaks at 129 and 275 °C may result from the presence of Ag_2O clusters inside or on the external surface of zeolite and 648 °C peak is attributed to isolated Ag^+ ions. In this work, therefore, broad ranged high temperature peaks appeared in low loading catalysts are thought to be from the isolated Ag^+ within zeolite framework and the mid-temperature peaks from the well-dispersed Ag_2O clusters (below XRD detection limit) within the pore or on the surface of zeolites.

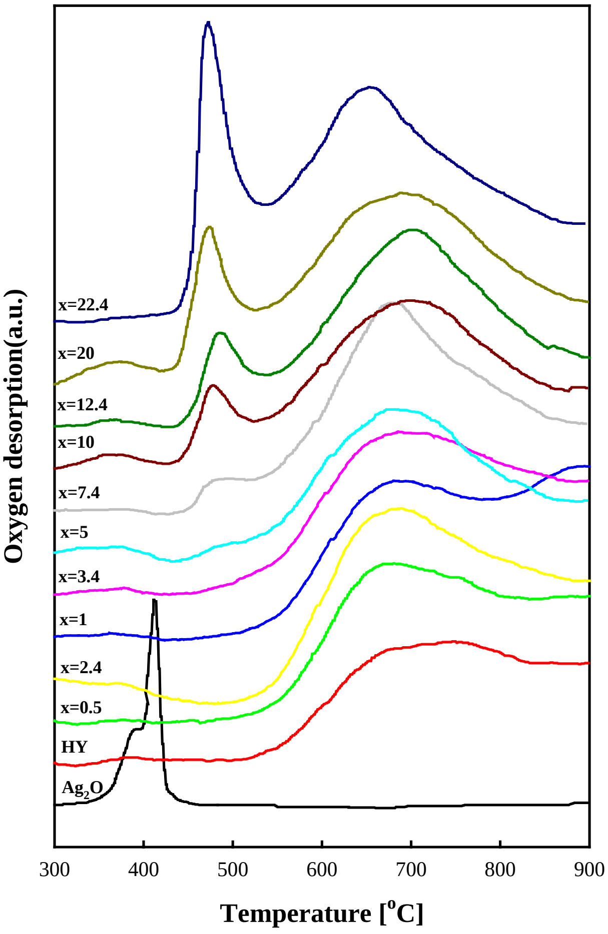

Fig. 7. O_2-TPD of Ag(*x*)/HY catalysts.

To find out the origin of the low temperature (100 °C) peak in TPR of Fig. 6, O_2-TPD was carried out under helium flow with the same pre-treatment as TPR. Fig. 7 shows the growing peak around 480 °C in O_2-TPD. The bulk Ag_2O liberated O_2 at about 400 °C, which is in accord with the temperature of Luo et al.'s experiment [18]. Higher desorption temperature (480 °C) of Ag(*x*)/HY catalyst compared to bulk Ag_2O implies that chemical state of the former is more stable than that of the latter. Therefore the peak at 480 °C might be due to the well-dispersed surface oxide species which interact with catalyst surface. Bethke and Kung [13] reported that the well-dispersed Ag_2O is more difficult to reduce than large Ag_2O particles.

Moreover, those well-dispersed surface oxide species was gradually increased with the fraction of metallic Ag phase. Note that the peak intensity at 480 °C increased with the silver loading, especially for the samples with detectable metallic Ag phase and there were neither the O_2-TPD peak at 480 °C nor the low temperature TPR peak at 100 °C for the low loading catalyst, $x \leq 3.4$, which showed no detectable metallic phase in XRD. From these results, it might be assumed that those well-dispersed surface oxide species is formed on to the metallic Ag surface or it is the partially oxidized metallic surface itself as confirmed by Kundakovic and Flytzani-Stephanopoulos [15] using XPS and UV–vis measurement.

Therefore it might be inferred that the presence of metallic Ag phase seems to play an important role to create silver oxide species or partially oxidized Ag surface onto the surface of metallic Ag phase under reaction condition, i.e., oxygen environment, and these silver oxide species might act as an active redox site during the oxidation reaction.

4. Conclusion

Dual functional adsorbent/catalyst system with both adsorption and catalytic function was suggested as an effective control method for the removal of low concentration VOC.

From the screening results obtained from adsorption, desorption and TPSR study, Ag/HY was selected as the best candidate for the dual functional adsorbent/catalyst system. HY has large adsorption capacity and unique desorption dynamics, such as low desorption temperature and narrow desorption temperature window, which might be advantageous for designing the continuous adsorption-regeneration cycling system.

Ag/HY catalyst showed the lowest conversion temperature for both toluene and MEK oxidation among other M/HY catalysts. Its catalytic activity was enhanced by increasing the Ag loading. The formation of metallic Ag phase was favoured with higher loading. TPR and O_2-TPD of Ag/HY catalyst suggested that the formation of partially oxidized species on the surface of metallic Ag should enhance the activity of Ag catalyst for the toluene oxidation.

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