Effect of loading sequence between Cu and Fe on SCR-C$_3$H$_6$ performance for Al-PILC based bimetallic catalysts

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Abstract. To investigate the effect of impregnation sequence on SCR-C$_3$H$_6$ performance, Al-PILC based catalysts with different impregnation sequences between Cu and Fe were prepared. Activity result showed that impregnation sequence influenced the SCR-C$_3$H$_6$ performance, where, the NO conversion followed the order from high to low: Cu-Fe/Al-PILC>FeCu/Al-PILC>CuFe/Al-PILC. XRD results indicated that the dispersion of the active phase was related to the impregnation sequence. The specific surface area was not the crucial factor affecting the activity. UV-Vis demonstrated that isolated Cu$_{2+}$ and Fe$_{3+}$ contributed to activity rather than CuO and Fe$_2$O$_3$ particles, and more isolated Cu$_{2+}$ and Fe$_{3+}$ existed on Cu-Fe/Al-PILC. H$_2$-TPR and XPS results revealed that superior reduction ability and more surface adsorbed oxygen led to the excellent SCR-C$_3$H$_6$ performance for Cu-Fe/Al-PILC catalyst.

1 Introduction

The emission of NOx rapidly increased, resulting from the increase in total energy consumption. As a result, it is harmful to the environment and human health [1], hence, it is urgent to remove NOx. Comparing the technologies for removal of NOx, SCR-HC is an efficient technology to remove NOx with application potential, due to the simultaneous removal of NOx and hydrocarbons without an external reducing agent [1-3].

In recent years, pillared interlayered clay (PILC), has been extensively used as a kind of excellent catalyst support to synthesize the supported catalysts for SCR-HC, due to its acidity, adjustable pore size, and high hydrothermal stability [4,5]. Great efforts were attached to exploring the influence of active metals on catalytic performance, from supporting single metal to co-loading multiple metals, and these metals include Cu, Ce, Fe, Co, Ag, and Pt, etc [6-9]. Regarding the catalysts supporting multiple metals, actually, the loading sequence of active components not only affects the formation of active species but also the redox properties [10,11]. By comparing the SCR-NH$_3$ performance over Cu-Fe-ZSM-5 and Fe-Cu-ZSM-5 catalysts prepared via the solid-state ion exchange method, Jouini et al. [12] claimed that the ion exchange sequence between Cu and Fe influenced the amount, degree of aggregation, and environment of obtained metal species, thereby leading to a difference in catalytic performance. Youn et al. [13] synthesized a series of M/V$_2$O$_5$/TiO$_2$ (M=W, Ce, Zr, and Mn) for SCR-NH$_3$ catalysts, apart from that, the catalysts with different impregnation order between M and V$_2$O$_5$ on TiO$_2$ support was also prepared for comparison, aiming to probe the effect on activity and N$_2$O yield of impregnation sequence. This result indicated that catalysts added W and Ce (W or Ce/V/TiO$_2$) showed the most active DeNOx properties at low temperatures. Additionally, the superiority of activity at low temperature for the vanadium firstly added catalysts (W or Ce/V/TiO$_2$) was due to the formation of...
more polymerized V_2O_5 on the sample. According to Sultana, among three catalysts, namely the subsequent exchange of Fe/ZSM-5 with copper (Cu/Fe/ZSM-5), the subsequent exchange of Cu/ZSM-5 with iron (Fe/Cu/ZSM-5), and co-exchange Fe-Cu/ZSM-5, Cu/Fe/ZSM-5 catalyst exhibited better SCR-NH_3 performance, due to its strong acidity and reducibility [14].

However, at present, there are relatively few studies to probe the effect of the impregnation sequence on the HC-SCR reaction. Consequently, based on our previous work [6], the impregnation sequence between Cu and Fe loaded on Al-PILC was investigated in this work, aiming to explore its influence on SCR-C_3H_6 performance.

2 Experimental

2.1 Synthesis of catalysts

In our previous study, the catalyst with the molar ratio of Cu/Fe of 0.13 (keeping the total metal loading of 20%) exhibited superior SCR-C_3H_6 performance. Hence, based on the molar ratio of Cu/Fe of 0.13, the catalysts with different impregnation sequences between Cu and Fe were prepared. Al-PILC support was synthesized using the method described in our previous paper [6].

FeCu/Al-PILC: Al-PILC support was impregnated into Fe(NO_3)_3 solution, and then the product was aged for 1 h after ultrasound for 4 h. After drying at 110 °C for 12 h, the sample was impregnated into Cu(NO_3)_2 solution, with ultrasound for 4 h and aging for 1 h, followed by drying at 110 °C for 12 h. Subsequently, the sample calcinated at 500 °C for 4 h to get the catalyst.

CuFe/Al-PILC: The synthesis process was similar to the FeCu/Al-PILC catalyst. However, the difference was that Al-PILC support was first impregnated into Cu(NO_3)_2 solution and then Fe(NO_3)_3 solution.

Cu-Fe/Al-PILC: The synthesis process was reported in our previous paper [6].

2.2 Catalytic activity measurements

The SCR-C_3H_6 performance evaluation over catalysts was conducted on a fixed-bed microreactor. 0.4 g catalyst was placed at the center of the quartz tube with an internal diameter of 6mm. Prior to each test, the sample was pretreated at 300 °C in N_2 atmosphere, followed by being fed the mixed gases consisting of 0.05% NO, 0.2% C_3H_6, 1% O_2, and He (as balance), at a total flow rate of 200 mL/min. The concentration of NO, NO_2, and NO_3 were detected using a flue gas analyzer (ECOM-J2KN, Germany), and a gas chromatograph (GC-4000A) with an FID detector was used to record the concentration of C_3H_6. The conversions of NO and C_3H_6, and N_2 selectivity were calculated using the equations in our previous paper [6].

2.3 Characterization

In this work, some techniques, e.g., N_2 adsorption-desorption, XRD, H_2-TPR, UV-Vis, and XPS were employed to probe the physical and chemical properties of catalysts. The characterization details can be referred in our previous paper [6].

3 Results and discussion

3.1 SCR- C_3H_6 performance evaluation

Fig.1 displays the SCR-C_3H_6 performance over these three catalysts. As can be seen from Fig. 1(a), apparently, in the temperature range of 150-550 °C, the NO conversion for these three catalysts followed the order from high to low: Cu-Fe/Al-PILC>FeCu/Al-PILC>CuFe/Al-PILC. Additionally, Cu-Fe/Al-PILC, FeCu/Al-PILC, and CuFe/Al-PILC catalysts achieved the maximum NO conversion of 93, 84, and 80%, respectively, at 250, 250, 300 °C. With a further increase in temperature, Cu-Fe/Al-PILC can keep NO conversion above 90%, whereas, FeCu/Al-PILC and CuFe/Al-PILC catalysts remained at 80% and 75%, respectively. This result indicates that the impregnation sequence affects the NO conversion, wherein, the catalyst prepared by co-impregnation exhibits superior
activity. In the case of N\textsubscript{2} selectivity (Fig. 1(b)), all of the catalysts achieved above 80% and followed the same order as NO conversion, suggesting the influence on N\textsubscript{2} selectivity caused by the impregnation sequence. From Fig. 1(c), as temperature increased, C\textsubscript{3}H\textsubscript{6} conversion increased gradually up to 100% at 400 °C. Comparing all catalysts, C\textsubscript{3}H\textsubscript{6} conversion of Cu-Fe/Al-PILC was higher than those of others. Based on the above SCR-C\textsubscript{3}H\textsubscript{6} performance, it can be induced that the impregnation sequences affect the SCR-C\textsubscript{3}H\textsubscript{6} performance, while the co-impregnation promotes the SCR-C\textsubscript{3}H\textsubscript{6} performance.

3.2 XRD
XRD patterns of all catalysts are displayed in Fig. 2. Regardless of the sequence of impregnation, no destroy occurred on the layered structure of montmorillonite, due to the appearance of characteristic peaks at 19.1 and 21.3°, ascribed to the two-dimensional (hk) crystal plane and the summation of hk indices (02) and (10) [15], respectively. Compared with other catalysts, Cu-Fe/Al-PILC synthesized by co-impregnation exhibited the weaker diffraction peaks of montmorillonite, which may be interpreted as that the coexistence compounds of copper and iron were easy to form, thereby enhancing the adsorption for X-rays [16]. Moreover, except for the Fe\textsubscript{3}O\textsubscript{4} phase at 2θ of 24.1, 33.1, 35.6, 40.8, 49.5, and 54.1°, the CuO phase was also observed at 2θ of 39.2° on Cu-Fe/Al-PILC catalyst. For the Fe\textsubscript{2}O\textsubscript{3} phase, the diffraction peak for CuFe/Al-PILC was stronger and shaper, which may be resulted from the continuous growth of the later-loaded iron species deposited on the surface of the first-loaded copper species. On the contrary, for FeCu/Al-PILC, the later-loaded copper species promoted the dispersion of the first-loaded iron species, resulting in a weaker and broader diffraction peak of Fe\textsubscript{2}O\textsubscript{3} [17,18]. According to the Scherrer formula, the crystallite size of catalysts was calculated as 19, 23, and 25nm for Cu-Fe/Al-PILC, FeCu/Al-PILC, and CuFe/Al-PILC, respectively. This result reveals that co-impregnation contributes to active species dispersing on the catalyst surface, because of the smaller crystallite size for the catalyst prepared by co-impregnation. This may be responsible for the superior SCR-C\textsubscript{3}H\textsubscript{6} performance for Cu-Fe/Al-PILC catalyst.
3.3 N$_2$ adsorption-desorption

Figure 3 shows the N$_2$ adsorption-desorption isotherms of catalysts, and the textural properties calculated are listed in Table 1. On the basis of IUPAC classification, these profiles belong to the type of IV, companying with the H3 hysteresis ring. This result indicates that these catalysts present mesopore, corresponding to the slit-like pores from lamellar particle material with a layered structure. This result also supports the fact that no destroy occurs on the layered structure of montmorillonite, which is in accordance with XRD. As can be seen from Table 1, no significant change appeared in the specific surface area for three catalysts, suggesting no apparent influence of impregnation sequence on the specific surface area. Note that there was an obvious difference in SCR-C$_3$H$_6$ performance, which demonstrates that the specific surface area is not a crucial factor affecting the denitrification efficiency.

3.4 UV-Vis

Table 1: Textural structure parameters of the catalysts.

| Catalysts       | $A_{BET}$ (m$^2$/g) | Pore volume $v$(cm$^3$/g) | Pore size $d$(nm) |
|-----------------|---------------------|--------------------------|------------------|
| CuFe/Al-PILC    | 82                  | 0.178                    | 8.36             |
| FeCu/Al-PILC    | 80                  | 0.177                    | 8.24             |
| Cu-Fe/Al-PILC   | 81                  | 0.194                    | 9.02             |

Fig. 2. XRD patterns of catalysts.

Fig. 3. N$_2$ adsorption-desorption isotherms of catalysts.
Fig. 4. UV-Vis spectra of catalysts.

Table 2 the quantitative analysis results of the UV-Vis.

| Samples         | Percentage/% |
|-----------------|--------------|
|                 | $A_1^a$ | $A_2^b$ | $A_3^c$ | $A_4^d$ | $A_5^e$ |
| CuFe/Al-PILC    | 1.9     | 15.6    | 33.8    | 41.9    | 6.8     |
| FeCu/Al-PILC    | 2.2     | 17.2    | 34.7    | 39.8    | 6.1     |
| Cu-Fe/Al-PILC   | 2.6     | 15.7    | 37.3    | 38.1    | 6.3     |

$^a$: Isolated Cu$^{2+}$ (~200nm);
$^b$: Isolated Fe$^{3+}$ (200-300nm);
$^c$: Fe$_3$O$_y$ clusters (300-400nm);
$^d$: Fe$_2$O$_3$ particles (>400nm);
$^e$: CuO (~700nm).

Fig. 4 presents the UV-Vis spectra of all catalysts. According to previous studies, the peaks in the regions of 200-300, 300-400, and >400 nm corresponded to isolated Fe$^{3+}$, Fe$_x$O$_y$ clusters, and Fe$_2$O$_3$ particles [19], while the respective peaks of isolated Cu$^{2+}$ and CuO clusters appeared near 200 and 700 nm [20]. After deconvolution and fitting of each spectrum, eight peaks can be got, denoted as I, II, III, IV, V, VI, VII and VIII. Among these peaks, I and VIII peaks can be ascribed to isolated Cu$^{2+}$ and CuO clusters, respectively, and others belonged to the Fe species. II and III peaks can be attributed to isolated Fe$^{3+}$, while IV and V peaks corresponded to Fe$_x$O$_y$ clusters. In addition, Fe$_2$O$_3$ particles can be indexed to VI and VII peaks. According to the area of peaks, the percentage of species can be calculated, as shown in Table 2. In terms of isolated Cu$^{2+}$, the respective percentage of CuFe/Al-PILC, FeCu/Al-PILC, and Cu-Fe/Al-PILC catalysts was 1.9, 2.2, and 2.6%, demonstrating the influence on copper species by impregnation sequence. Cu-Fe/Al-PILC catalyst had the most isolated Cu$^{2+}$, which was responsible for the high activity at low temperature, since Cu$^{2+}$ as an active phase can effectively adsorb NO [21]. In addition, compared with Cu-Fe/Al-PILC, more Fe$_2$O$_3$ particles (A4) were formed on catalysts prepared by sequential impregnation, increasing the content of 38.1% for Cu-Fe/Al-PILC to 39.8% for FeCu/Al-PILC and 41.9% for CuFe/Al-PILC. On the contrary, the percentage of Fe$_x$O$_y$ clusters decreased. This result suggests that the impregnation sequence also affects the iron species. A previous study reported that Fe$_x$O$_y$ clusters were an important active phase for SCR reaction [15]. Therefore, the activity of catalyst may be relative to isolated Cu$^{2+}$, Fe$^{3+}$, and Fe$_2$O$_3$ clusters, whereas, Fe$_2$O$_3$ particles and CuO clusters have no significant promotion in SCR reaction [19].
3.5 H$_2$-TPR

The H$_2$-TPR profiles of catalysts are displayed in Fig. 5. After deconvolution, two reduction peaks ($\beta_1$ and $\beta_2$) respectively appeared in the range of 190-200°C and 230-250°C over catalysts, which belonged to the H$_2$ consumption owing to isolated Cu$^{2+}$ and CuO, respectively [22]. Based on relative reports, three different reduction peaks ($\alpha_1, \alpha_2, \alpha_3$) observed in the region of 300-800 °C were ascribed to the stepwise reduction of Fe species. The $\alpha_1$ peak was ascribed to the reduction of isolated Fe$^{3+}$, while $\alpha_2$ peak corresponding to the reduction of FeO$_x$ clusters and/or FeO$_x$ particles [6]. Subsequently, the reduction of Fe$_2$O$_4$ to Fe$^0$ occurred above 600°C ($\alpha_3$) [2,3,19]. Interestingly, compared to CuFe/Al-PILC and FeCu/Al-PILC catalysts, all reduction peaks ($\alpha_1, \alpha_2, \alpha_3$) of the iron species for Cu-Fe/Al-PILC catalyst moved toward lower temperatures. In our previous studies, the interaction between Cu and Fe can promote the reduction of Fe species, due to the fact that copper can dissociate H$_2$ to atomic H and overflow H atoms to Fe$^{3+}$, resulting in promoting the reduction of Fe$^{3+}$ at a lower temperature [2,6]. Therefore, it can be induced that co-impregnation contributes to the interaction of Cu and Fe. Moreover, among these catalysts, the reduction of copper species ($\beta_1$ and $\beta_2$) for FeCu/Al-PILC and CuFe/Al-PILC respectively appeared at the lowest and highest temperatures. This result may be because the impregnation sequence of Cu affects the probability of direct contact between copper species and H$_2$ [18]. Conversely, loading Fe after Cu did not shift the reduction of iron species to lower temperature, due to the difficulty in reduction resulted from the continuous growth of iron species deposited on copper species, in agreement with XRD. When Fe was first loaded, the copper species facilitated the dispersion of Fe species, resulting in a lower reduction temperature of Fe species for FeCu/Al-PILC than that for FeCu/Al-PILC. Considering the catalytic activity, Cu-Fe/Al-PILC catalyst exhibits the best activity due to its superior reduction ability.

3.6 XPS

Figure 6 displays the XPS spectra of O1s. By deconvolution, two types of oxygen species can be distinguished, surface adsorbed oxygen (denoted as O$_a$) and lattice oxygen (O$_b$), appearing in the regions of 531.4-531.9 and 529.1-529.7 eV, respectively. As is well known, surface adsorbed oxygen was the active oxygen species, owing to its high mobility. As a result, on one hand, the oxidation of NO to NO$_2$ was promoted [23]. On the other hand, the peroxydic ion O$_{2-}$ can effectively participate in the reaction of hydrocarbons [24]. According to the area of peak, the calculated ratios of O$_a$/O$_b$ were illustrated in Fig. 6. As can be seen, among the three catalysts, Cu-Fe/Al-PILC had the most surface adsorbed oxygen. This phenomenon was because of the formation of more oxygen vacancies and unsaturated chemical bands on Cu-Fe/Al-PILC surface, due to the strong interaction between Cu and Fe caused by co-impregnation [25]. However, owing to the weak interaction between Cu and Fe on catalyst prepared by sequential impregnation, there was difficulty for Cu$^{2+}$ and Fe$^{3+}$ in entering into each other crystal lattice to substitute, thereby affecting the formation of oxygen vacancies [19]. Taking into consideration the SCR activity, the high SCR activity can be attributed to the high content of surface adsorbed oxygen.
4 Conclusions

Three Al-PILC based catalysts, Cu-Fe/Al-PILC, FeCu/Al-PILC, and CuFe/Al-PILC, were prepared to investigate the effect of impregnation sequence on SCR-C$_3$H$_6$ performance. Activity results showed that the impregnation sequence influenced the catalytic activity, where, Cu-Fe/Al-PILC synthesized via co-impregnation exhibited the highest NO conversion of 93% at 250 °C. Several characterizations revealed that Cu-Fe/Al-PILC catalyst exhibited excellent SCR-C$_3$H$_6$ performance, due to its superior reduction ability, more isolated Cu$^{2+}$ and Fe$^{3+}$, and more surface adsorbed oxygen. In addition, the specific surface area was not the crucial factor affecting the activity.

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