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Preparation of modified γ-alumina as stationary phase in gas–solid chromatography and its separation performance for hydrogen isotopes

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Abstract On the basis of impregnation method, several stationary phases were prepared using γ-Al_2O_3 with the solution of transition metal salts and the breakthrough curves of gas chromatograph for H_2 isotopes were analyzed under the temperature of liquid nitrogen. The effects of carrier gas, flow rate and doping concentration on the separation performance for H_2 and D_2 were systematically investigated. The overall results showed that the surface areas and adsorptive capacities of modified γ-Al_2O_3 were slightly lower than unmodified one while the separation performance and symmetry of chromatographic peaks of the former were more excellent. In addition, the chromatographic peaks of ortho- and para-H_2 were no longer separated and the retention time shortened to half on columns of modified γ-Al_2O_3. All the magnetic transition metal ions modified γ-Al_2O_3 did very well for the separation of H_2/D_2 under the conditions of neon as carrier gas with a flow rate of 60 mL/min and column lengths of 1.0 m and injection amounts of 0.1 mL. Especially, the $MnCl_2$ modified γ-Al_2O_3 exhibited the best performance for separating H_2/D_2 with an optimum doping concentration of 20 wt%.

Keywords Gas chromatography · Hydrogen isotope separation · γ-alumina · Adsorption · Impregnation

1 Introduction

Hydrogen is one of the most abundant elements on Earth while less than 1 % is present as molecular hydrogen gas H_2 (Schlapbach and Züttel 2001). The overwhelming majority is chemically bound as H_2O in water and some is bound to the liquid or gaseous hydrocarbons. Nowadays, many scientists and engineers are convinced that H_2 is a desirable energy source because it is renewable and its usage would reduce the emission pollution (Zhao et al. 2004; Nikitin et al. 2008; Murray et al. 2009; Wang and Yang 2010). The heavy isotope of H_2, D_2, is not only an important raw material for future nuclear industry but also one of core elements of moderator for fission reaction. Moreover, it can be used as a tracer in the fields of chemical reaction, medicine, and geographic science. Thus, searching for a suitable storage/separation carrier for H_2 isotopes receives research interest following the increasing attention paid to the green alternative and nuclear energy. The concentration of D_2 in a natural composition of H_2 isotopes is very small coupled with the fact that the separation and purification of H_2 isotopes has always been a hot topic (Fukada and Fujiwara 2000; Naik et al. 2001; Darkrim et al. 2002; Wang and Bhatia 2009a, b; Deng et al. 2012) for relevant scientists around the world. So, how to detect and analyze accurately on the concentration of H_2 isotopes are critical issues. Currently, the production for H_2 isotopes is mainly via various isotopes separation techniques, including cryogenic distillation, proton exchange, centrifugation, and electromagnetic mass spectrometry (Esswein et al. 2010). In addition, several methods such as mass-spectrometry, nuclear magnetic resonance spectroscopy, and gas chromatography (GC) have been used for analyzing H_2 isotopes in laboratory (Peng et al. 2011). Among them, the GC method with a cryogenic column is

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one of the most extensively used methods in analyzing H_2 isotopes for its accurate quantification and simplicity in terms of operation, construction and maintenance. Besides, it can be even used to recover small quantities of T_2 from exhaust gas employing the valve-switching technique with multiple intermittent cyclic operations (Zhou et al. 2006). Thus, it is not difficult to imagine that the GC method is very meaningful for the separation, purification and on-line analysis of H_2 isotopes.

The principle for separating H_2 isotopes via GC method is mainly based on the gas–solid adsorption/desorption, utilizing the small difference of mass and dispersion force between H_2 isotopes. It is well-known that the heterogeneity of particle size, morphology and the extent of filling tightness of the stationary phase in column will endow it with a multi-path effect to some extent which will have great impacts on the separation performance of chromatography (Yang et al. 2008), indicating that a proper selection of the stationary phase is very important for a typical separation process. Of late, several packing materials such as γ-Al_2O_3 (Moore and Ward 1958, 1960; Hunt and Smith 1961; Kawamura et al. 2000a, 2001; Samsun et al. 2001; Fukada et al. 2002; Chu et al. 2006; Wang et al. 2011; Naik et al. 2012), Pd–Pt alloy (Fukada et al. 1995), zeolites (Naik et al. 2001; Kawamura et al. 2000b, 2008; Kotoh et al. 2002; Degtyareva and Bondareva 2004; Zhang et al. 2006), glass microsphere and activated carbon (Stanciu et al. 2001; Schell et al. 2012) have been reported in literatures and employed as the GC stationary phases for analyzing H_2 isotopes. Among them, γ-Al_2O_3 has attracted the greatest attention due to reasons such as its good performance on radiation, high porosity and effective ability to work at low temperatures (Kawamura et al. 2000a, 2001; Chu et al. 2006; Naik et al. 2012). The separation of H_2 isotopes using metal oxides coated γ-Al_2O_3 materials as the stationary phase has been studied by several research groups (Moore and Ward 1958, 1960; Hunt and Smith 1961; Kawamura et al. 2000a, 2001; Chu et al. 2006; Wang et al. 2011; Naik et al. 2012). All of the reported results have indicated that this kind of materials has an excellent performance for separating H_2 isotopes. Unfortunately, there are few reports on the effects of doping concentration and different metal oxides on the separation performance of H_2 isotopes, to the best of our knowledge, and let alone the comparative studies of adsorptive properties for the stationary phase materials before and after its modification.

From this viewpoint, we have used the $MnCl_2$ modified γ-Al_2O_3 materials in the present work to analyze the separation performance of H_2 isotopes as the functions of loadings and operation parameters. In addition, other transition metal ion modified γ-Al_2O_3 materials were also used as the stationary phases to evaluate the separation performance.

2 Experiments

2.1 Apparatus and materials

The reconstructed GC2060 gas chromatograph (Lunan Analytical Instrument Ltd, China) equipped with a thermal conductive detector and N2000 chromatograph data working station (Zhejiang University) was applied in the entire analysis process. Gas samples of Ne, He, and H_2 with purities above 99.999 % were provided by Qingdao Heli Gas Co., Ltd, China. D_2 with purity of 99.9 % was provided by Tianjin Vista Technology Co., Ltd, China. Solid samples of γ-Al_2O_3 (60 ~ 80 mesh, Fengying Molecular Sieving Manufacturing Co., Ltd, China) were used in the present work. Chlorides of Cr, Mn, Fe, Co, Ni and Cu with purities above 99 % (Sinopharm Chemical Reagent Co., Ltd) were used as modified reagents. It is noteworthy that we enabled manual control injection via a six-way valve and a quantitative tube (0.1 mL) to improve the accuracy of gas injection.

The operation conditions of GC used in the present work were as follows: The modified γ-Al_2O_3 column was used as the separation column and a stainless steel column (2 m length × 3 mm i.d.) packed with Porapak Q (50–80 mesh, Waters Co., Milford, USA) was used as the reference column; bridge current was 80 mV and the temperature of detector was 80 °C. The breakthrough curves of GC for H_2 and D_2 were analyzed under the temperature of 77 K. The N_2 sorption measurements were carried out at 77 K on a static volumetric sorption analyzer (ASAP2020, Micromeritics). H_2 adsorption measurements were performed with an Intelligent Gravimetric Analyzer (IGA-001, Hiden), which is an ultrahigh vacuum, clean system and incorporates a microbalance capable of measuring weights with a resolution of ± 0.1 µg (Zhao et al. 2004). Before adsorption measurement, samples were evacuated for 7 h at 200 °C under vacuum. The microscopic structural features of modified γ-Al_2O_3 were evaluated via X-ray powder diffractometer (XRD, Bruker D8 with CuKα radiation), confocal laser Micro-Raman spectrometer (LabRAM HR UV-NIR, HORIBA Jobin–Yvon), and field-emission scanning electron microscopy (SEM, Hitachi S4800).

2.2 Preparation of the column packing materials

Transition metal ions modified γ-Al_2O_3 were prepared via an impregnation method with the corresponding solution of chloride (Chu et al. 2006). In a typical process of Al_2O_3 coated with manganese ions, 2.5 g $MnCl_2$ were dissolved in a mixture solution of 20 mL water and 5 mL ethanol and then 5 g γ-Al_2O_3 were added with stirring. The resulting mixture was stirred for 12 h in dark at room temperature and later evaporated in a rotary evaporator until solution dried. After that, the coated γ-Al_2O_3 was dried in a vacuum oven for 10 h at 120 °C and the divalent manganese modified γ-Al_2O_3 was therefore obtained. The modified materials were ground and sifted to 80 ∼ 100 mesh and then filled into a stainless steel column (1 m length × 3 mm i.d.). The column was subjected to an aging treatment at 250 °C for 4 h for the first use under a flow rate of 30 mL/min of He through the column.

3 Results and discussion

3.1 Influence of carrier gas

We first studied the chromatographic peaks of H_2 isotopes with He and Ne as carrier gas at a flow rate of 60 mL/min on the column of $MnCl_2$ modified γ-Al_2O_3, as shown in Figs. 1 and 2, respectively. It is worth noting that we have settled a unified injection time (1 min) for ensuring an effective comparison of chromatographic peaks. From the two charts, we can see obviously that all the chromatograms have a shoulder peak at the position of around 1.0 min which is deemed to be a dead volume peak. Chromatograms in He are slightly more skewed than the ones in Ne under similar conditions. In addition, the output of this shoulder peak is opposite in Ne and He, ascribing to the difference of thermal conductivity between injection gas and carrier gas.

According to the comparison of Figs. 1 and 2, we can find that an effective separation of H_2 and D_2 (40 %H_2–60 %D_2) can be achieved using Ne and He as the carrier gas, however, the signal sensitivity of H_2 isotopes in Ne is much higher than the one in He. Moreover, the retention time of H_2 isotopes shortened to half in comparison of γ-Al_2O_3 and the modified one packed columns, and the symmetry of peak was slightly improved when Ne was used as the carrier gas. The combination of above results made us to believe that Ne is more suitable to serve as a carrier gas for the separation and quantitative-analysis of H_2 isotopes. In addition, we noticed that there are two chromatographic peaks for pure H_2, indicating that the column of γ-Al_2O_3 used in the present experiment will enable the split of H_2, that is, the separation of ortho-H_2 and para-H_2. However, the split of chromatographic peaks will definitely affect the accurate quantitative analysis of H_2 isotopes in our future work to some extent. On the other hand, modified γ-Al_2O_3 via impregnation with $MnCl_2$ can greatly accelerate the conversion from para- to ortho-H_2 (Cunningham and Johnston 1958; White and Lassettre 1960). The two peaks of ortho-H_2 and para-H_2 obviously turned into a single one coupled with the features of symmetric shapes and shortened retention time, which

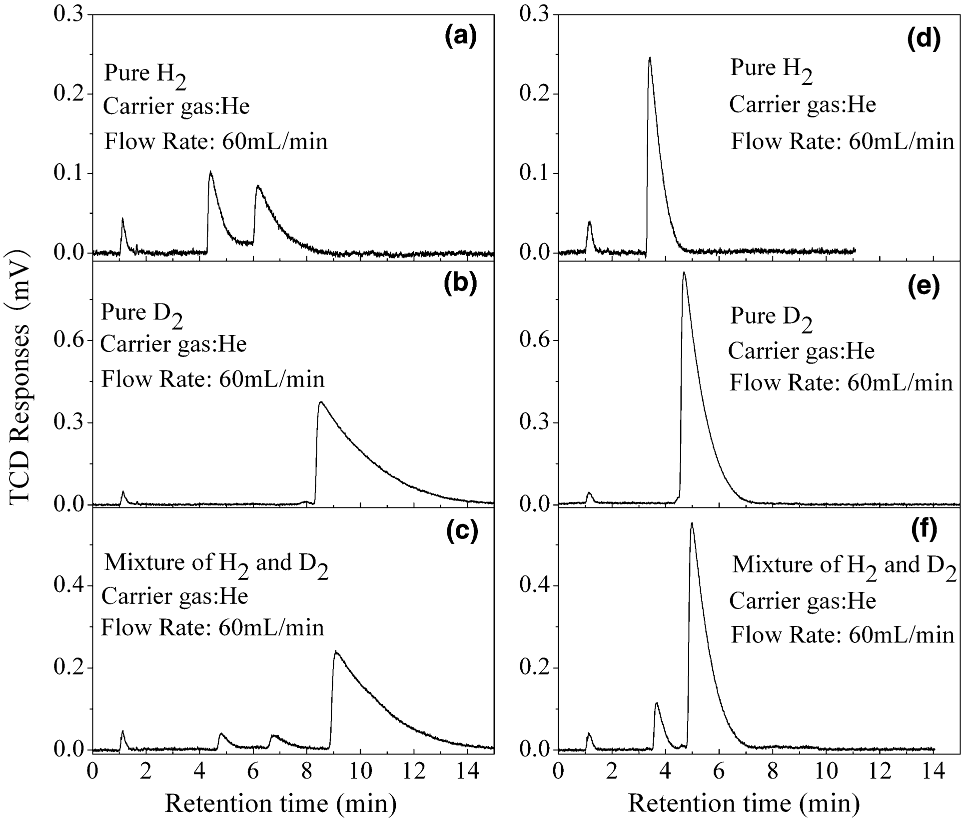

Fig. 1 The chromatograms of H_2, D_2 and the mixture of both on the columns of unmodified γ-Al_2O_3 (**a**, **b**, **c**) and 20 wt% $MnCl_2$ modified γ-Al_2O_3 (**d**, **e**, **f**) using He as the carrier gas with a flow rate of 60 mL/min

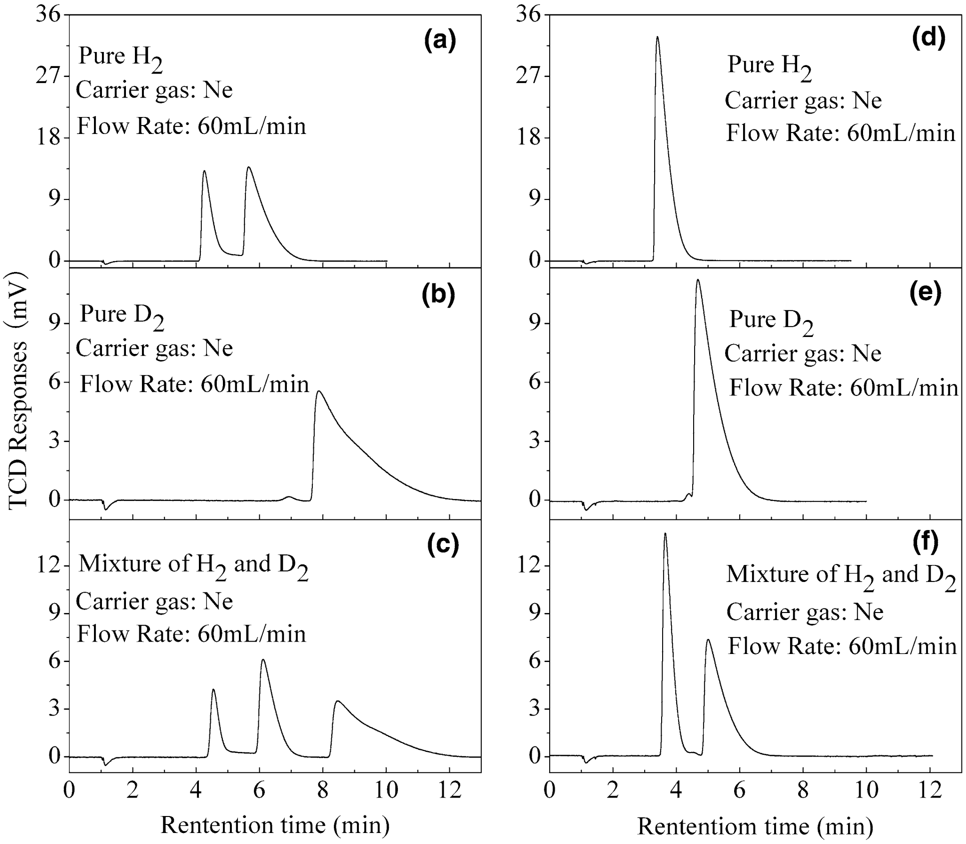

Fig. 2 The chromatograms of H_2, D_2 and the mixture of both on the columns of unmodified γ-Al_2O_3 (**a**, **b**, **c**) and 20 wt% $MnCl_2$ modified γ-Al_2O_3 (**d**, **e**, **f**) using Ne as the carrier gas with a flow rate of 60 mL/min

would probably be favorable for an accurate quantitative analysis and rapid on-line analysis of H_2 isotopes in mixture.

3.2 Influence of the flow rate

The influence of flow rate on the chromatographic peaks mainly lies in two aspects of peak shape and retention time and thereby affects the separation performance of components in a mixture. The variation trends of the retention time for H_2 and D_2 under different flow rate of Ne are shown in Fig. 3. It can be clearly seen from Fig. 3 that both the retention times of the two components and the difference between them increases as the flow rate decreases. The separation performance for H_2 and D_2 apparently becomes better with a reduction of flow rate which is really beneficial to get D_2 with high purities. However, the retention time greatly lengthens and the width of chromatographic peaks slightly increases (Inset in Fig. 3) as the flow rate decreases. In addition, the shape of peaks always deteriorates as flow rate decreases for the occurrence of strong adsorption, especially for D_2, which will not allow an accurate quantification. Although the reduction of flow rate can enhance the separation performance of H_2 and D_2, the whole operation period becomes longer which will be surely detrimental to improve the working efficiency. Moreover, the altitude of peak breakthroughs is also affected by the flow rate of carrier gas, in which the height of peaks increases gradually with the reduction of flow rate. This is maybe due to the fact that the TCD is one of the concentration sensitive detectors and the injection gas has

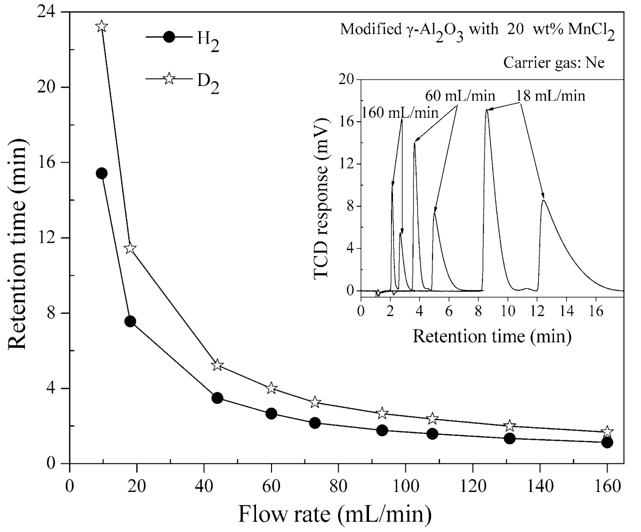

Fig. 3 The relationship between the retention times of H_2 and D_2 on the column of 20 wt% $MnCl_2$ modified γ-Al_2O_3 materials and the flow rate of carrier gas (neon)

been eluted from thermal conductivity pool with a larger flow rate before its equilibrium. When the flow rate of Ne was set at 60 mL/min, the peak resolution (R_s) of H_2/D_2 can reach a value of 1.64 according to the common formula for calculating resolution, $R_s = 2(t_2 - t_1)/1.7(w_{0.5,\ 1} + w_{0.5,\ 2})$, where t_1 and t_2 are retention times of the peaks of interest, and $w_{0.5,\ 1}$ and $w_{0.5,\ 2}$ are peak widths measured at the half height (Snyder et al. 1997; Kehimkar et al. 2013). The overall results of shape and width of chromatographic peaks, retention time and resolution have been able to meet the requirements of separation performance and on-line analysis.

3.3 Influence of Mn^{2+}-doping concentration

It is well-known that the doping concentration of metal ions is an important factor for a specific carrier which will affect the existing form and reaction performance of metal ions on the surface of adsorbents. In order to investigate the effects of loadings on the separation performance of H_2 isotopes, we tested the chromatographic peaks of H_2 isotopes in a mixture gas under the same experimental conditions. Relationship between the difference of retention times in H_2 and D_2 and the loadings of $MnCl_2$ was shown in Fig. 4. We can clearly notice that the difference of retention times for H_2 and D_2 shows an increase trend first and then decrease, indicating that the separation performance is relevant to loadings. The difference in retention time increases with increasing the loadings and reaches a maximum value at about 20 wt% and then decreases drastically at a higher content, that is, the concentration dependence of separation performance shows a concentration quenching effect (Cai et al. 2011, 2012a).

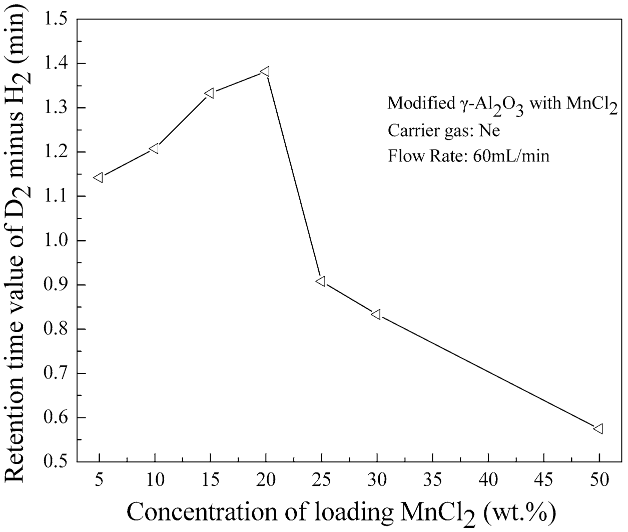

Fig. 4 The difference values of the retention time between H_2 and D_2 on the column of $MnCl_2$ modified γ-Al_2O_3 as a function of doping concentration

The SEM images of modified γ-Al_2O_3 with different loading concentration of $MnCl_2$ in Fig. 5 indicated that a proper loading can greatly enhance the heterogeneities of particle size, which would be beneficial to the separation performance of H_2/D_2 in chromatography (Wang et al. 2011). In addition, XRD patterns and Raman spectra shown in Fig. 6 further confirmed the transformation of adsorbent's structure. For example, the γ-Al_2O_3 materials modified with 20 wt% $MnCl_2$ have already showed some Mn-related weak diffraction peaks in XRD patterns (Fig. 6a) and a characteristic Raman Mn–O–H stretching band at around 3,400 cm^{-1} (Li et al. 2009) has appeared in Raman spectra (Fig. 6b). The overall results of SEM, XRD, and Raman spectra indicated that excessive loadings of $MnCl_2$ will affect the uniformity and structure of γ-Al_2O_3, which will reduce the adsorptive capacity of H_2 due to the reduction of activated adsorptive sites on the surface of γ-Al_2O_3 (Fig. 7). We believe that some physical interactions exist between adsorbed molecules and adsorbent, on top of that, weak electronic interactions maybe also exist between the adsorbed H_2 isotopes and metal (or chloride)

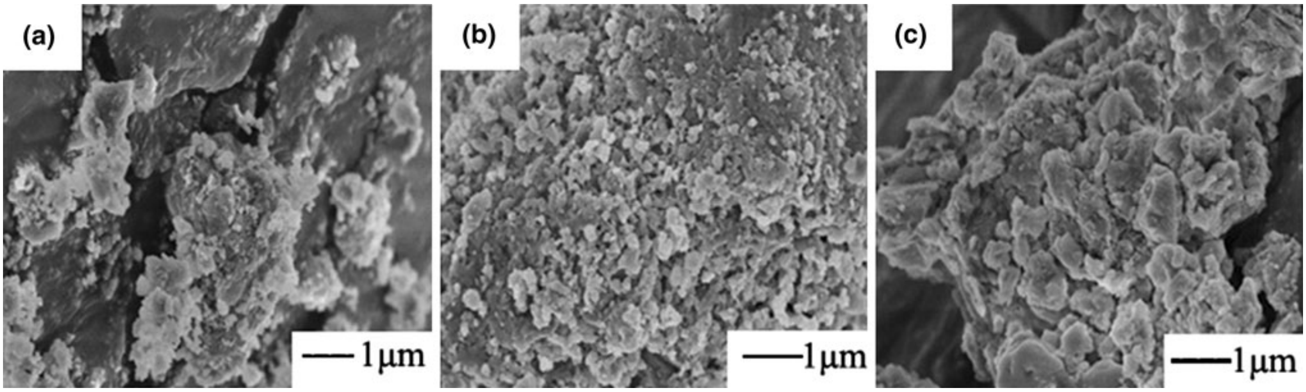

Fig. 5 SEM images of the stationary phase materials used in our experiments. (**a** γ-Al_2O_3, **b** 20 wt% $MnCl_2/Al_2O_3$, **c** 50 wt% $MnCl_2/Al_2O_3$ materials)

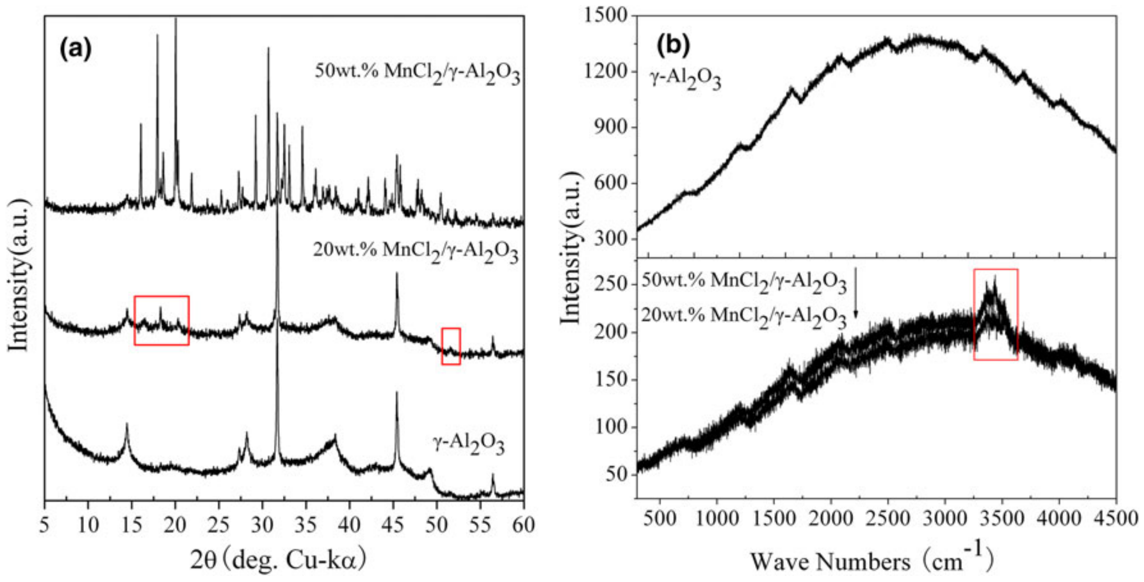

Fig. 6 **a** The XRD patterns of the representative samples used in our experiments. **b** Raman spectra of the stationary phase materials, γ-Al_2O_3 and modified ones

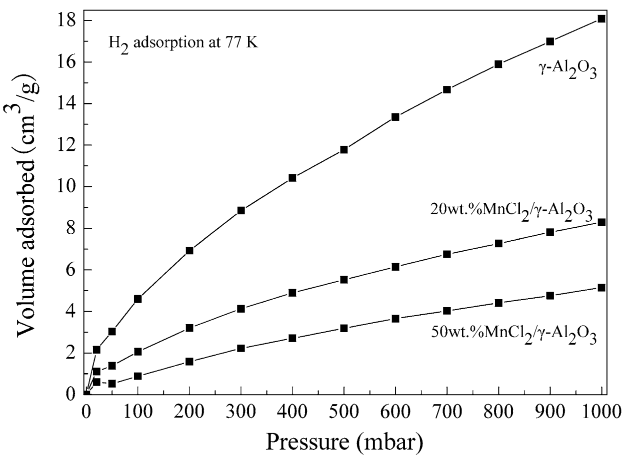

Fig. 7 Adsorption isotherms of H_2 on the stationary phase materials at 77 K and 1 *bar*

ions loaded on the surface of γ-Al_2O_3. Therefore, changes in the trend of difference between the retention times of H_2 and D_2 (Fig. 4) may be expected as results of synergistic effects between physical and electronic interactions.

The N_2 sorption isotherms at 77 K on the γ-Al_2O_3 doped with different concentration of $MnCl_2$ were shown in Fig. 8. Isotherms of all samples are of type IV in the IUPAC classification scheme (Sing et al. 1985), typical for mesoporous materials. Loadings of $MnCl_2$ have basically no impacts on the shape of isotherms while greatly lower the adsorptive capacities. Moreover, modified γ-Al_2O_3 materials have similar pore size distributions (PSDs) determined from the N_2 adsorption data with the Barrette–Joynere–Halenda (BJH) method (Inset in Fig. 8) (Liao et al. 2012). The decrease of adsorptive capacities is ascribed to the fact that both the surface area and pore volume of γ-Al_2O_3 gradually decrease with an increase in the doping concentration of $MnCl_2$. The values of surface area (m^2/g) and total pore volume (cm^3/g) varied from 218.8 and 0.386 for initial γ-Al_2O_3 to 78.2 and 0.163 for the sample impregnated with 50 wt% $MnCl_2$, respectively. A desorption hysteresis is observed on all samples when the relative pressure (p/p_0) reaches a value of 0.45, indicating that the capillary condensation effect occurred in mesopores. In addition, the adsorbed volume increases relatively slow with an increase of relative pressure, indicating that samples have a wide PSD (1.7–57 nm), in relation with PSD pattern. We can find that the impregnated $MnCl_2$ has little effects on PSDs and the dominated pore size for all samples is nearly located at 7.3 nm.

3.4 Separation performance of coating different metal ions

The Fig. 9 is the chromatograms for H_2 and D_2 on the columns of γ-Al_2O_3 modified with different transition metal ions. The chromatographic peak of H_2 on the column of γ-Al_2O_3 splits into two peaks of ortho- and para-H_2. Moreover, the retention time of D_2 is much longer than ortho-H_2 while retention time of para-H_2 is slightly shorter than ortho-H_2, indicating that difference of physical adsorption strength on the surface of γ-Al_2O_3 exists among these three molecules (Li et al. 2011). The separation performance is explained as being principally due to a hindered rotation in typical pores of γ-Al_2O_3 for different quantum energy states (Sandler 1954; White and Lassettre

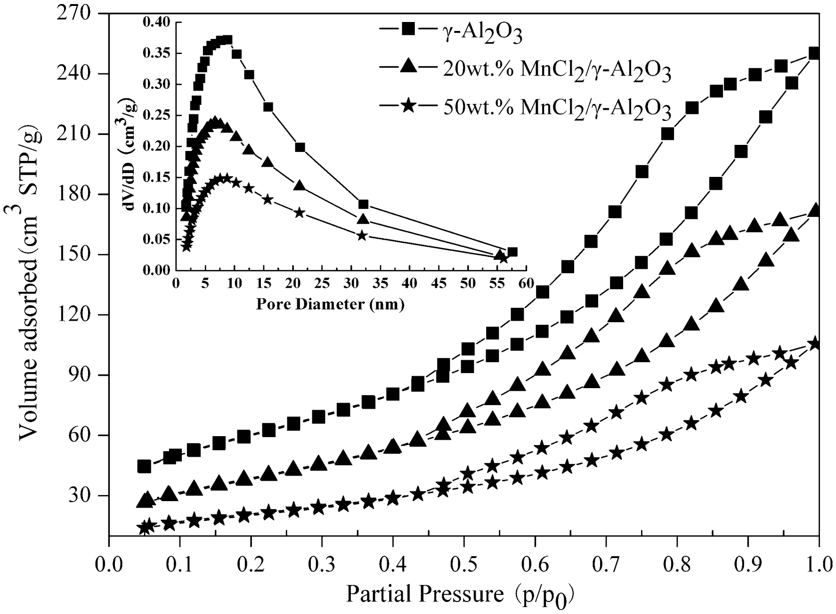

Fig. 8 The nitrogen adsorption–desorption isotherms of γ-Al_2O_3 and modified γ-Al_2O_3 with different contents of $MnCl_2$ (*Inset chart* is the pore size distributions of these materials)

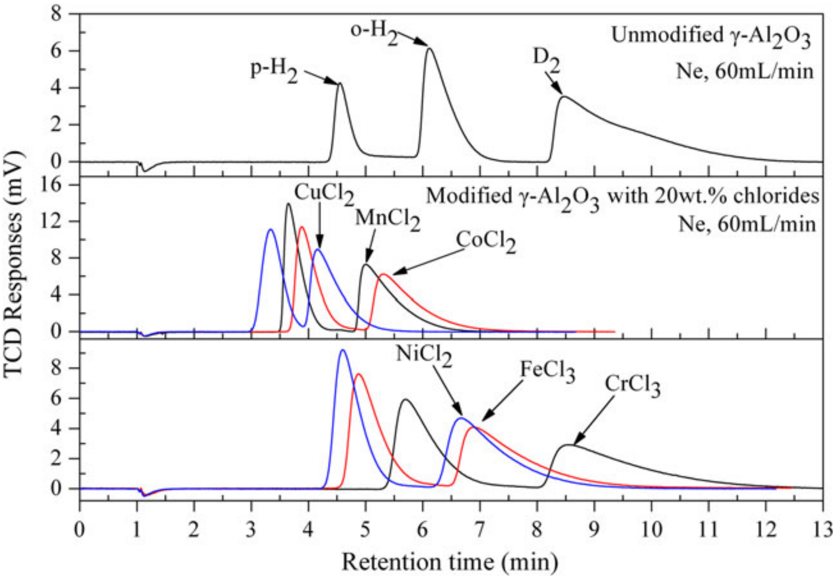

Fig. 9 The chromatograms of H_2/D_2 mixture on the columns of γ-Al_2O_3 and modified γ-Al_2O_3 with different kinds of chlorides at the doping concentration of 20 wt%

1960; Zhao et al. 2005; Grinev et al. 2007), that is, the equilibrium quantum sieving effect (Beenakker et al. 1995; Cai et al. 2012b).

It is worth noting that the chromatographic peak of H_2 is only a single one with slightly asymmetry on the column of modified γ-Al_2O_3, showing that modified γ-Al_2O_3 can accelerate the conversion from para-H_2 to ortho-H_2 and these magnetic transition metal ions act as catalysts for this conversion (Cunningham et al. 1958; Cunningham and Johnston 1958; Li et al. 2010, 2011). All of the modified γ-Al_2O_3 can achieve the separation of H_2 isotopes and shorten the retention time to a certain extent via the combination effects of both equilibrium quantum sieving and magnetic catalysis. The effect of transition metal ions on the separation performance seems to have something to do with the kinds of metal ions used in our present work. We find that the retention times of H_2 and D_2 on columns of modified γ-Al_2O_3 with odd number electrons in its 3*d* orbitals of transition metals (Cu, Co and Mn), for instance, are much shorter than the ones with even number electrons (Fe, Cr and Ni). This special behavior in respect to the retention time could originate from electronic properties of different metal ions on the surface of γ-Al_2O_3 and detailed work will be done in our future study. In addition, there are different energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of adsorbed H_2 isotopes and metal (chloride) ions loaded on the surface of γ-Al_2O_3 (Johnson et al. 2010; Lau et al. 2011). The difference in the degrees of matching for the symmetry of frontier molecular orbitals between the adsorbed molecules and metal ions will also affect separation performance on the base of the frontier orbital theory. From the results, we can concluded here that the column of γ-Al_2O_3 modified with proper contents of $MnCl_2$ or $CoCl_2$ exhibits the best separation performance in view of the retention time and peak resolution for H_2/D_2 in Fig. 9. The modified γ-Al_2O_3 packing materials maybe have potentials to replace noble metal Pd for the separation of H_2 isotopes which will greatly reduce the costs of separation and show great prospects for engineering applications.

4 Conclusion

It is feasible to achieve the separation of H_2/D_2 on the column of γ-Al_2O_3 under certain conditions by a cryogenic GC. Overall results indicate that γ-Al_2O_3 will greatly shorten the retention time and slightly improve the symmetry of peaks when it was modified with some transition metal ions, showing good selectivity and high separation efficiency for H_2 isotopes. However, the chromatographic peak of H_2 is apparently only symmetric depending greatly on the metal ion used to modify γ-Al_2O_3. The surface area and adsorptive capacities of modified γ-Al_2O_3 are slightly lower than that of the unmodified one while the separation performance of the former is more excellent, indicating that the separation performance of porous material is not proportional to the adsorptive capacity. In addition, it is of paramount importance that the conversion rate for ortho- and para-H_2 can be greatly enhanced on the surface of modified γ-Al_2O_3, exhibiting great potential significance for investigating the conversion mechanism and exploring the production and storage methods for H_2 with particular relevance on the eve of H_2 fuel era.

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