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VOCs adsorption by modified MCM-41 and a new way to recycle adsorbents

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Abstract MCM-41 was modified by ion exchange of nickel and the adsorptive property was examined using ethylene and *n*-butane as the representatives of VOCs. The adsorption capacity for *n*-butane barely changed after modification. The isosteric heat of *n*-butane adsorption at different coverage was calculated through Clausius–Clapeyron equation and it increased only a little. After modification the maximum adsorption amount for ethylene was 0.59 g $g_{adsorbent}^{-1}$ at 308 K up to 10^5 Pa. The adsorption capacity was much higher than former reported adsorbents. A possible mechanism was proposed. After thermal treatment, Ni^+ ion formed and became the active center of ethylene polymerization. Carbon chain lengths of the final products were limited to the sizes of molecular sieves. Catalytic polymerization and adsorption was considered as a new route for ethylene adsorption. We also declared a new way to recycle the adsorbents by washing with organic solution.

Keywords VOCs · *n*-Butane · Ethylene · Ni/MCM-41 · Catalytic polymerization and adsorption

1 Introduction

Emissions of Volatile Organic Compounds (VOCs) can cause air pollution and bring harm to human health at even a very low concentration (Foster et al. 1992; Dimotakis et al. 1995). Catalytic or thermal oxidation, absorption, adsorption, filtration, membrane and condensation are the common techniques to remove VOCs (Khan and Ghoshal 2000; Vorontsov et al. 2000; Ruddy and Carroll 1993). Among all the treatments, adsorption is one of the choices referring to the global shortage of resources. It's also easy to operate and the cost is low (Qu et al. 2009). A well-performed adsorbent can be used in traffic tunnel, underground parking area, traffic hub, indoor and some other places.

The siliceous microporous and mesoporous materials, such as MCM-41, MCM-22, MCM-48, SBA-15, attract a great deal of attentions because of their possible uses as catalytic supports or adsorbents (Coasne et al. 2006; Denayer et al. 2006; Choudhary and Mantri 2000; Serrano et al. 2004). As an important member of the family of silicate mesoporous materials, MCM-41 was first discovered by Mobil in 1992 (Beck et al. 1992). MCM-41 possesses hexagonally packed arrays of one-dimensional cylindrical pores with large surface area and pore volume (Kresge et al. 1992). In consideration of the large internal surface area, easily controlled and uniformity of pore size, high thermal and hydrothermal stability, MCM-41 is believed to be an excellent adsorbent (Shim et al. 2006; Zhao et al. 2001).

Since the lack of noble metals, transitional metals which are relatively rich become the hot spot of the catalysis studies. Materials containing nickel are known to be effective catalysts in lots of important industrial manufacturing processes. Many researches are also based on the catalytic characteristic of nickel, such as selectively NO_x reduction (Mosqueda-Jiménez et al. 2003), methane reforming with carbon dioxide (Liu et al. 2009), catalytic growth of carbon fibers from methane and ethylene (Takehira et al. 2005), conversion of ethylene to propene and butene (Iwamoto and Kosugi 2007), hydrogen sorption (Park and Lee 2010;

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Moradi et al. 2010; Prasanth et al. 2010), and so on. But the adsorption property of adsorbents modified with nickel for gaseous VOCs has not been investigated so far.

In our study, nickel was chosen as the modified element for ion exchange. After the modification we investigated the adsorptive properties for *n*-butane and ethylene, which were chosen as the representives of VOCs.

2 Experimental

2.1 Materials and modification

MCM-41 with a Si/Al ratio equaling to 30 was ordered from Novel Chemical Technology Co., Ltd. *n*-butane and ethylene with the purity of 99.995 % and Nickel (II) nitrate hexahydrate (analytical grade) were used without further treatment.

1 g MCM-41 was added into 0.1 mol L^{-1} nickel nitrate solution. Then the solution was heated up to 353 K with magnetic stirring for 6 h. It took 3 times for full ion-exchange. After filtrated and washed with deionized water, the powder was dried at 378 K for 12 h. The sample was finally calcined in air at 823 K for 8 h and denoted as Ni/MCM-41.

2.2 Adsorption measurements of nitrogen, *n*-butane and ethylene

The nitrogen isotherms and pore size distribution of the samples were measured at 77 K using a gas adsorption measuring apparatus, Belsorp mini II, BEL Japan, Inc. The samples were degased at 673 K under vacuum (below 10^3 Pa) for 3 h before measurement. The surface area was obtained with the Burunauer–Emmett–Teller (BET) method. The pore size distribution was calculated on the basis of adsorption branch using the Barrett–Joyner–Halenda (BJH) method and Micro-Pore (MP) method. The *n*-butane and ethylene isotherms were also obtained from Belsorp measurements. The pretreatment was same as nitrogen adsorption. But the measuring temperature was around room temperature (308 K).

2.3 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra were recorded by a Thermo Nicolet 380 spectrometer (USA) with a resolution of 4 cm^{-1}. The wafer was compressed with the sample and KBr, in which the mass ratio of sample to KBr was about 1:100.

2.4 Gas chromatography and mass spectrometer (GC–MS)

GC–MS analysis was performed on a Finnigan TRACE DSQ GC/MS, Thermo, USA. A 30 m × 0.25 mm capillary column with a 0.25 μm film thickness (DB-17MS, Agilent, USA) was equipped in the GC 2000. The injector temperature was 523 K. The GC oven was programmed firstly from 323 to 373 K at 10 K min^{-1} with initial holding time of 1 min, then holding at 373 K for 2 min, secondly from 373 to 523 K at 20 K min^{-1} with final holding time of 1 min. The mass spectrometer was operated with an ionization voltage of 70 eV and a source temperature of 523 K.

3 Results and discussion

3.1 Characterization of the samples

Figure 1 shows the N_2 adsorption and desorption isotherms of MCM-41 before and after modification by Ni ions. For convenient observance, the isotherms of Ni/MCM-41 were elevated vertically by 200 cm^3 g^{-1}. They all presented a type IV isotherm with obvious hysteresis loops. This result indicated that pore structure didn't change before and after the ion-exchange. Figure 2 shows the pore size distribution calculated by BJH method and MP method. As shown in the illustration, we can observe that the pores mainly distributed in the range of 1–5 nm. Ni ions are larger than Na ions in diameter. So the introduction of Ni ions might change the pore volumes to a certain extent. After the modification, the volume of micro pores ($r < 2$ nm) decreased, while mesopores ($2 < r < 50$ nm) barely changed. This result indicated that the introduced Ni ions mainly existed in the micro pores. We also confirmed that the surface area ($S_{\text{MCM-41}} = 855.35$ m^2 g^{-1}, $S_{\text{Ni/MCM-41}} = 854.71$ m^2 g^{-1}) barely altered. All the results proved that the skeleton structure of the pores did not change significantly.

3.2 *n*-Butane adsorption and desorption measurements

Figure 3 depicts the *n*-butane adsorption and desorption isotherms at 308 K. The isotherms of Ni/MCM-41 were elevated vertically by 10 cm^3 g^{-1} for convenient observance. The maximum adsorption amounts of *n*-butane for MCM-41 and Ni/MCM-41 were actually almost the same: for MCM-41 was 43.72 cm^3 g^{-1}, while for Ni/MCM-41 was 44.70 cm^3 g^{-1}. The introduction of Ni ion did not enhance the adsorption of *n*-butane, but it also did not destruct the pore system.

To study the adsorption system in a thermodynamic way, we use Clausius-Clapeyron equation to estimate the isosteric heat of adsorption. The equation is commonly written as

$$\Delta H_{\text{ads}} = -R\partial(\ln p)/\partial(1/T) \quad (1)$$

where ΔH_{ads} denotes isosteric heat of adsorption in kJ mol^{-1}. P means the equilibrium pressure in bar. T is the

adsorbent temperature in Kelvin and R is the gas constant equaling to 8.3145 J mol^{-1} K^{-1}. Isotherms of n-butane adsorption were obtained at 308, 318, 328, 338 and 348 K. Then, we could get the isosteric heat of n-butane adsorption by calculating the slope of the linear line, which showed the relationship between pressure and temperature variations during isosteric heating. The adsorption of n-butane could be regarded as monolayer adsorption. By fitting with Langmuir model, we calculated the monolayer maximum volumes of adsorption (V_m) at room temperature, which was about 200 cm^3 g^{-1} for both MCM-41 and Ni/MCM-41. The coverage was defined as the specific value of adsorption amount to V_m. The maximum calculable coverage was less than 15 % in the temperature range of 308–348 K, so we calculated the isosteric heat of adsorption below 15 % coverage and the results were summarized in Table 1. (Adsorption is an exothermic

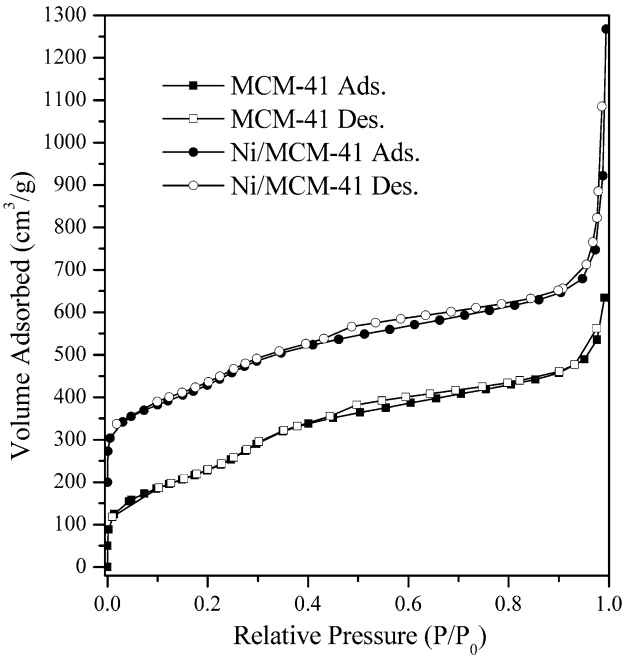


Fig. 1 Adsorption-desorption isotherms of nitrogen at 77 K on MCM-41 and Ni/MCM-41

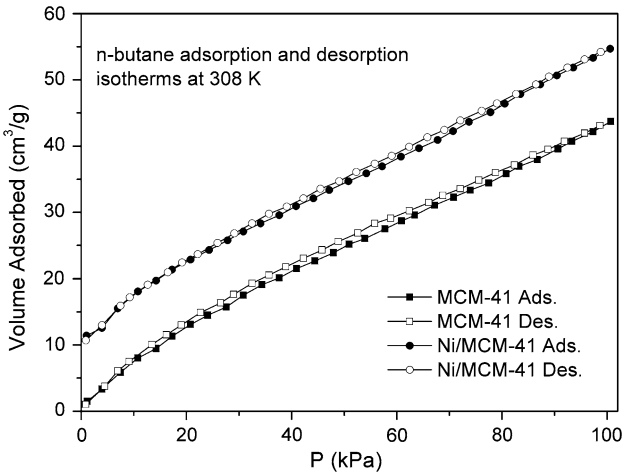


Fig. 3 Adsorption-desorption isotherms of n-butane at 308 K on MCM-41 and Ni/MCM-41

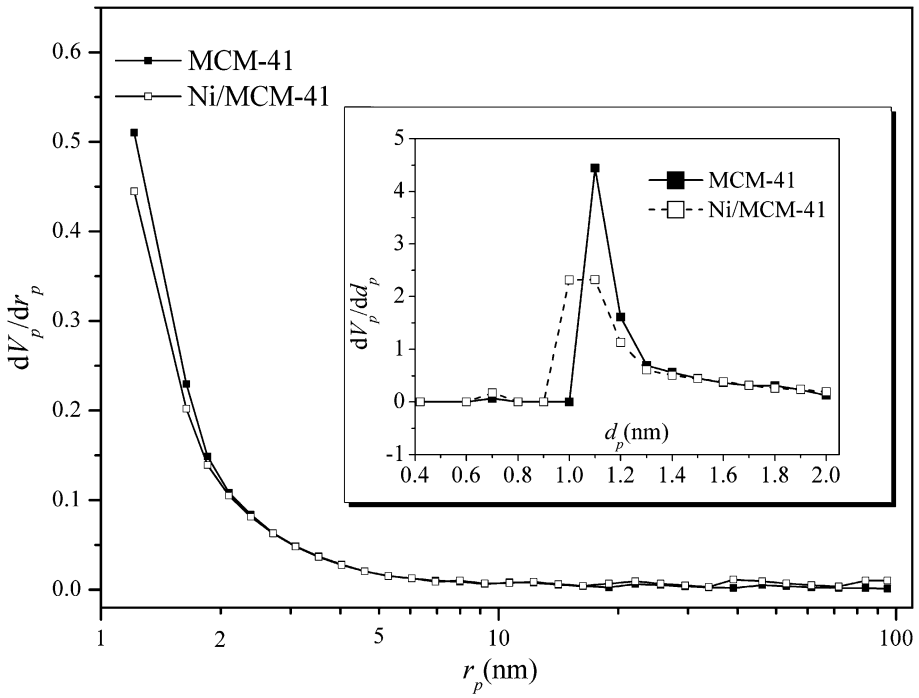


Fig. 2 Pore size distribution of MCM-41 and Ni/MCM-41 calculated in BJH method. The *insert graph* is calculated in MP method

Table 1 Isosteric heats of *n*-butane adsorption at different coverage

	Isosteric heats of adsorption at different coverage (kJ mol^{-1})		
	6 %	10 %	14 %
MCM-41	25.72	25.12	23.89
Ni/MCM-41	26.52	26.42	26.16

process, but it is customarily noted as positive value.) From Table 1, we can observe that the isosteric heat of *n*-butane increased only a little after modification. So Ni ions did not obviously enhance the interaction between the surface of adsorbent and *n*-butane molecules. It was also confirmed that the isosteric heat of *n*-butane adsorption reduced with the increased coverage.

3.3 Ethylene adsorption and desorption measurements

Activated carbon (AC), which owns highly developed surface and great pore volume, is often used as a well-performed adsorbent. During the measurements of ethylene adsorption, we used AC to make a comparison, which having a BET surface area of more than 1,200 $m^2\ g^{-1}$. Figure 4a shows us the results. The maximum capacity of adsorption for AC is about 70 cm^3 (STP) g^{-1} and most of the ethylene molecules desorbed during the period of desorption.

Figure 4b, c are the ethylene adsorption and desorption isotherms of MCM-41 before and after the modification, respectively. From the isotherms, we can observe that 1 gram MCM-41 could adsorb only 13 cm^3 (STP) ethylene at most before the modification. Most of the ethylene molecules desorbed as the pressure went down, which means the molecules were physically adsorbed. Figure 4c shows the isotherms of Ni/MCM-41. An apparent improvement of adsorption capacity can be observed from the isotherms. The maximum value is 472 cm^3 (STP) g^{-1}. That is 0.59 $g_{ethylene}\ g^{-1}_{adsorbent}$, which is seven times higher than activated carbon. It is also much higher than other adsorbents announced in the literatures (Erdoğan et al. 2008; Patdhanagul et al. 2010; Sue-Aok et al. 2010). Few molecules desorbed after the desorption measurement, which means the adsorbates were chemically adsorbed on Ni/MCM-41. After the adsorption and desorption measurement, we denoted the samples as C_2H_4–Ni/MCM-41.

3.4 FTIR and GC–MS studies on C_2H_4–Ni/MCM-41

In order to investigate the adsorption in molecule level, we took the spectrum of C_2H_4–Ni/MCM-41. The results are shown in Fig. 5. After the adsorption of ethylene, few new bands emerged. The peak of water (around 1,630 cm^{-1})

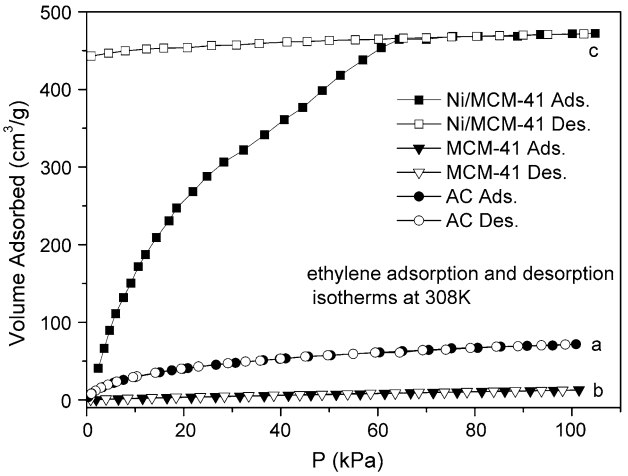


Fig. 4 Adsorption-desorption isotherms of ethylene at 308 K on *a* AC, *b* MCM-41 and *c* Ni/MCM-41

still existed. The new peaks are: 2,960 cm^{-1} (belonging to the antisymmetric stretching vibration of methyl groups); 2,930 cm^{-1} (belonging to the antisymmetric stretching vibration of methylene groups); 2,872 cm^{-1} (belonging to the symmetric stretching vibration of methyl groups and methylene groups); 1,465 cm^{-1} (belonging to the bending vibration); 1,380 and 1,365 cm^{-1} (belonging to double symmetric bending vibrations of methyl groups pertained to isopropyl groups) (Socrates 2001). From the introduction of methyl groups and isopropyl groups, we can conclude that the chemical adsorption was caused by ethylene polymerization. No more peaks were observed during the FTIR measurements which means that no other species of products were found besides hydrocarbons.

In order to identify the chain length of the polymers formed on Ni/MCM-41, we used *n*-hexane to strip the adsorbates and GC–MS to analyze the polymers. The results are shown in Fig. 6. It was confirmed that olefins, in which decene (C_{10}) and docacene (C_{12}) were the main products, were formed in the Ni/MCM-41 sample. The *n*-hexane which used only as the solvent was not reactive, while Ni ions should be responsible for the polymerization. The polymerization performs as long as Ni ions are present in regardless of containing solvent or in gas phase system. Because it belongs to the basic nature of the absorbent modified by Ni ions.

3.5 Possible mechanism for ethylene adsorption onto Ni/MCM-41

After the modification of MCM-41, the Ni/MCM-41 adsorbed H_2O from the air. During the vacuum treatment at high temperature, H_2O reacted with Ni^{2+} to form Ni^{+} and H^{+} as following equation (Dooryhee et al. 1991; Azuma and Kevan 1995; Kasai et al. 1978):

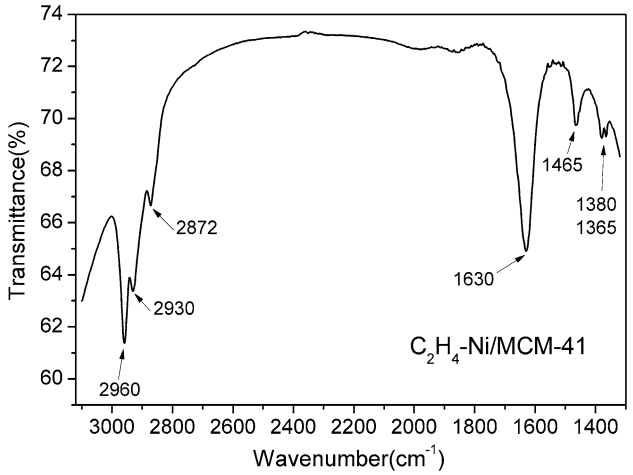


Fig. 5 The FTIR spectrum of C_2H_4–Ni/MCM-41 at 308 K

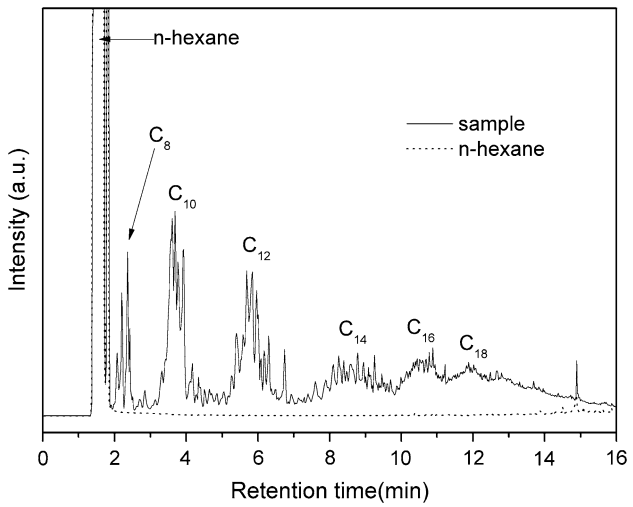
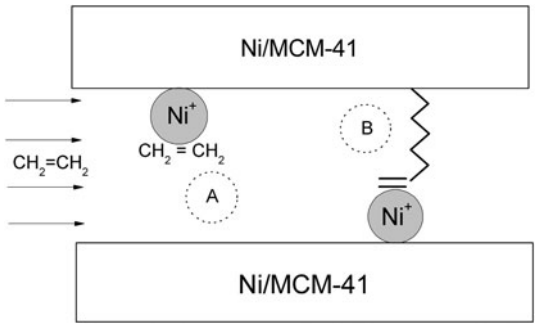


Fig. 6 The GC–MS spectrum of solution samples extracted from Ni/MCM-41 after the adsorption of ethylene at 308 K

$$2Ni^{2+} + H_2O \rightarrow 2Ni^{+} + 2H^{+} + {}^{1}/_{2}O_2 \quad (2)$$

The Ni^{+} acted as active sites for ethylene adsorption. Scheme 1 shows the possible mechanism of adsorption of ethylene according to our results. Phase A shows the initial adsorption of one ethylene molecule onto the Ni^{+} site. When the second ethylene molecule reached the active site, dimerization occurred and the C_4 olefin formed. At the Ni^{+} site, the unsaturated carbohydrates also could isomerize and form different isomers. When more ethylene molecules polymerized, what presented in Phase B might happen. Owing to the restriction of the diameter of the pore canal, the carbon chain couldn't get longer. Here we calculated the length of C_{10} polymers as 1.2 nm, which is close to the size of most pores (1–1.2 nm by MP or <2 nm by BJH) showed in Fig. 2. Therefore, we believe that the polymers produced and adsorbed mainly in the micro pores. The ethylene molecules



Scheme 1 Possible mechanism for adsorption of ethylene on Ni/MCM-41 in our study

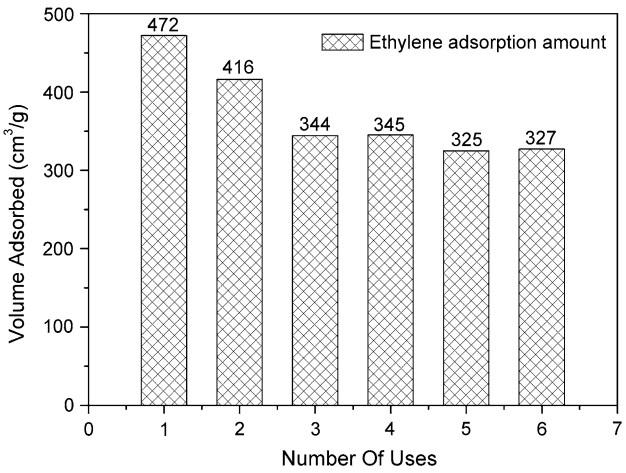


Fig. 7 The results of repeated ethylene adsorption on the same adsorbent

had enough time to diffuse to every active site during our measurements and reach the maximum adsorption capacity. So the final products depend on the pore size. Our scheme only shows the linear chain olefins for the convenience. In fact, isomers of the olefins with branched chains also followed the rules.

3.6 A new way to recycle adsorbents for ethylene adsorption

Comparing to the traditional concept of adsorption, catalytic polymerization and adsorption could be regarded as a new concept for adsorption. Small molecule adsorbates polymerized into big ones and were adsorbed by adsorbents. The catalytic polymerization and adsorption of ethylene in our research was such a good example. Especially the final adsorbates were olefins with high carbon number, which were considered as fuels. Through GC–MS tests, we declared a new way to recycle the final adsorbents. We used organic solution (*n*-hexane) to transfer the products into the liquid phase after adsorption, which led to an easy operation. Then the adsorbents were ready for next

adsorption process. We simulated the recycle process and reused the same adsorbent for several times. The results are shown in Fig. 7. We can observe that the adsorption capacity of the adsorbent decreased a few every time after the recycle. But after a few times of reuse, it could remain an adsorption capacity of more than 300 $cm^3\ g^{-1}$, which was still much higher than other adsorbents. More importantly, the adsorbent could regain an adsorption capacity of about 350 $cm^3\ g^{-1}$ after nickel ion-exchange once, even when the adsorbent was almost deactivated.

4 Conclusion

In this paper, we modified MCM-41 by Ni ion exchange and studied the adsorptive properties for *n*-butane and ethylene. After modification, the adsorption amount for *n*-butane increased a little, which caused by the slight enhancement of isosteric heat. But during the measurements of ethylene adsorption, Ni ions played an important role. Ni/MCM-41 was able to adsorb 0.59 g ethylene for per gram sample at 308 K. After the measurement of adsorption, the samples were analyzed by FTIR and GC–MS. All the results revealed the fact that ethylene polymerized at the active sites of Ni/MCM-41. The final main products were olefins with high carbon numbers, such as C_{10} and C_{12} olefins and their isomers. They were all confirmed by GC–MS and FTIR measurements. The possible mechanism for ethylene adsorption onto Ni/MCM-41 was proposed. Ethylene molecules would dimerize at the Ni^+ active sites and make the carbon chain grow two by two. Because of the limit of the pore size, the carbon chain would stop growing finally. Catalytic polymerization and adsorption was proposed as a new concept for adsorption. By washing with organic solution, we also declared a new way to recycle the adsorbents for ethylene adsorption.

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