Evaluation of the catalytic surface of Ni Impregnated-meso-microporous silica KIT-6 in CH₄ dry reforming by inverse gas chromatography

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Abstract

Inverse gas chromatography (IGC) was employed in evaluating the catalytic surface of meso-microporous KIT-6 impregnated Ni (0.5–2.0 wt%) in methane dry reforming reaction.

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The free energy of adsorption did not change significantly for the sample modified with highly dispersed Ni species (0.5 wt%). At higher Ni loadings, higher free energy of adsorption and enthalpy of adsorption of the probes were observed, together with high dispersive interaction and specific interaction of aromatics. The results indicated that during the impregnation, Ni species preferably penetrated into the microporous region to form Ni particles and became 'unaccessible'. This feature was used to understand the dependence of activity on Ni loading for the gas phase catalytic methane reforming with carbon dioxide on Ni/KIT-6. The lower TOF at low metal loadings was attributed to Ni particles located in the micropores which result in diffusional constraint of reactants and products.

Keywords: Inverse gas chromatography; KIT-6; surface property, dry reforming; Ni; methane

Introduction

Nickel containing catalysts have been intensively investigated as they catalyzed many interesting and industrially important reactions [1-6]. Ni-loaded SBA-15, La₂O₃-SBA-15, and mesoporous ZSM-5 catalysts demonstrated high catalytic activity in CH₄ reforming with CO₂ [1-2,4]. Also, Ni-loaded ZrO₂ showed good catalytic performance in phenol hydrodeoxygenation [5], and small Ni particles (≤ 4 nm) dispersed on Al₂O₃ promoted effectively the hydrogenation reaction of benzene ring [6]. KIT-6, a mesoporous silica, has been reported recently to possess a high surface area, a well-ordered (cubic *Ia3d* symmetry)

structure, a large pore volume, and an adjustable pore diameter (4-12 nm) [7]. It is composed of two sets of interpenetrating mesoporous channels interconnected by microbridges [7,8]. The microbridges (*ca.* 1.8 nm from N₂ adsorption/desorption using DFT model) are ordered and interconnect two main mesoporous channels of KIT-6 on the 3-fold axis (Fig. 1) [8]. Although there is much interest on the catalytic property of metal containing mesoporous catalysts [1-3,9-11] and the ordered three-dimensional structure of KIT-6 [7,8,12-21], there are no detail studies on the catalytic surface property of the meso-microporous silica KIT-6 impregnated with Ni, especially with regard to the location of the metal or the areas the probe molecules interact.

Inverse gas chromatography (IGC) has been used extensively to study adsorption and surface property of solid materials [22]. Using a probe molecule, it provides thermodynamic parameters, surface energy, reaction kinetics, textural, and acid/base information of solid surfaces [23-36], such as polymers [23,24], fibres [25,27], adsorbents [30], catalysts [31-34], molecular sieves [35,36], etc. In our previous study, IGC was employed to investigate the effect of the pore structure on KIT-6's surface property. By size exclusion, the probes were able to penetrate into the main mesoporous channels but unable to access the micropores [36]. This prompted us to examine the size effect of Ni nanoparticles on the surface properties of mesostructured cellular foam (MCF), which is a mesoporous silica with no micropores. We observed that the highly dispersed Ni particles on MCF promoted specific interaction with the benzene ring of the aromatic hydrocarbon probes [33].

In this article, we used IGC to obtain structure-reactivity relationship in the CO₂ reforming of CH₄ on Ni/KIT-6, a material with both micropores and mesopores. The free energy of adsorption, enthalpy of adsorption, and the specific and dispersive components of

the surface free energy were derived for KIT-6 samples modified with different amounts of Ni. From the IGC analysis, the amount of Ni accessible to probe molecules of different dimension and different nature were calculated. After that, the catalysts were tested in methane dry reforming with carbon dioxide. The surface property obtained from IGC gives insight to the ‘unexpected’ catalytic activity on highly dispersed Ni species.

2. Experimental

2.1 Catalysts preparation

KIT-6 was prepared according to previous literatures [7,8,36]. Typically, 6 g of Pluronic P123 triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, Aldrich) was dissolved in concentrated HCl (11.8 g, 37 wt%) and distilled water (217 g), and then *n*-butanol (6 g) was introduced. After 1 h stirring at 308 K, tetraethyl orthosilicate (TEOS, 12.9 g) was added. The mixture was stirred for another 24 h at 308 K and then hydrothermally treated in an autoclave at 373 K for 24 h. The filtered product was dried and calcined at 773 K for 3 h in air to remove the copolymer template. KIT-6 supported nickel catalysts were prepared by impregnating the support with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution dropwise to yield the nominal metal content. After drying under an infrared lamp, the catalyst was calcined in air at 573 K for 30 min and then reduced in 10% H_2/Ar at 773 K for 60 min.

2.2. Characterization of the materials

Small-angle XRD analysis was performed on a Rigaku D/MAX-rB diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda=0.15418$ nm). Wide-angle X-ray diffraction (XRD) patterns were obtained with a Rigaku D/MAX-IIA diffractometer with $\text{Cu-K}\alpha$ radiation. N_2

adsorption/desorption measurements were carried out on a Micromeritics Tristar-3000 (Quantachrome) apparatus at 77 K. Prior to the measurement, the samples were degassed at 523 K for 3 h. BET method was used to measure the surface area, and BJH model was employed in evaluating the pore size distribution. Transmission electron microscopy (TEM) measurements were carried out on a JEOL JEM-2011 transmission electron microscope. Each sample was mounted on a carbon-coated copper grid by drying a droplet of an ethanol suspension of the ground sample on the grid.

The reducibility of nickel species over the catalyst was characterized by H_2 temperature-programmed reduction (H_2 -TPR) using a Micromeritics Chemisorb 2720 apparatus. A sample of 50 mg was heated to 473 K under a He flow and maintained for 2 h. After cooling to 373 K, the stream was switched to 10% H_2 /Ar with a flow rate of 50 mL min^{-1} , and H_2 -TPR was carried out with a linear heating rate of 3 K min^{-1} from 373 K to 1123 K. The dispersion of Ni on KIT-6 was determined by temperature-programmed desorption (TPD) of H_2 on a GC112A gas chromatography (Shanghai Precision and Scientific Instrument Co. Ltd., China). Before the experiments, the catalysts were purged with Ar at 773 K for 60 min, and the then catalyst was cooled down to 313 K. Pure hydrogen was introduced into the sample cell at 313 K until no more adsorption was recorded, i.e. saturation. Afterwards, the gas phase and physisorbed hydrogen were removed by argon purging until the thermal conductivity detector (TCD) signal at the reactor exit returned to the baseline. H_2 desorption was conducted at a heating rate of 20 K min^{-1} from room temperature to 1073 K. The blank test of KIT-6 showed no adsorbed hydrogen. The dispersion of nickel was calculated based on the amount of H_2 desorbed from the sample,

assuming each exposed metal atom adsorbs one hydrogen atom [37]. The nickel dispersion was calculated as following,

$$D \% = 2 \times m_{H_2(\text{desorption})} / m_{Ni(\text{impregnating})} \times 100\% \quad (1)$$

where D represents Ni dispersion, $m_{H_2(\text{desorption})}$ represents the mole of the hydrogen desorption from the sample and $m_{Ni(\text{impregnating})}$ represents the mole of Ni loading.

2.3 IGC apparatus and procedure

IGC was performed on a GC112A gas chromatography (Shanghai Precision and Scientific Instrument Co. Ltd., China) equipped with a flame ionization detector. A stainless steel column (i.d. 2 mm × 300 mm) containing 0.2 g of 60-80 mesh reduced catalyst was installed in the GC oven. Retention data was collected on a workstation (Shanghai Wuhao Information Technology Co. Ltd., China). High purity nitrogen ($\geq 99.999\%$) was used as the carrier gas at an optimum gas flow of ca. 28 mL·min⁻¹. The inlet pressure p_i and the outlet column pressure p_o , measured by precision manometers, were used to correct the net retention volume (Eq. 2) [22,32,38-41] using the James-Martin factor (Eq. 3).

$$V_N = Fj(t_R - t_d) \left(\frac{p_0 - p_w}{p_0} \right) \left(\frac{T}{T_{meter}} \right) \quad (2)$$

where t_R is the retention time, t_d , the dead time, p_w , the vapor pressure of water at the soap bubble flowmeter, T_{meter} the ambient temperature, and j , the James-Martin compressibility factor defined as:

$$j = \frac{3}{2} \left[\frac{(p_i / p_0)^2 - 1}{(p_i / p_0)^3 - 1} \right] \quad (3)$$

The probes used were a series of *n*-alkanes (*n*-C6 to *n*-C9), cyclohexane,

trichloroethylene, tetrachloroethylene, benzene, and toluene (analytical reagent grade, Shanghai Chemical Reagents Company). Prior to the tests, the column was stabilized in the GC oven at 513.2 K overnight under nitrogen flow. After that, the relative humidity (RH) inside the column was kept low and constant, and identical for each measurement. To obtain the appropriate retention time of the probes, all measurements were carried out in the temperature interval of 463.2-493.2 K. The amounts injected were less than 0.1 μL to minimize solute-solute interaction so that the retention time only reflected the catalyst-probe interactions. Furthermore, the isotherm using the chromatographic peak maxima (PM) method [40] falls onto a straight line (regression coefficients ≥ 0.990) with the amount injected from 0.05 μL to 0.5 μL , indicating that every measurement was conducted in the Henry's law region. Methane was used as a nonsorbing gas to determine the dead time t_d , which was used to correct the net retention volume V_N . The retention time of each probe can be distinguished from the dead time of methane (Fig. S1 and Table S1). In each test, three repeat injections were conducted to obtain the average net retention volume. The chromatogram of the probes in Fig. S1a shows a good symmetry, indicating the adsorption sites were relatively uniform on the investigated solid surface [20,32,38-40].

2.4 Models and calculations

2.4.1. Standard free energy of adsorption

The standard free energy of adsorption at infinite dilution ΔG_{ads} ($\text{J}\cdot\text{mol}^{-1}$) is given by the following equation: [33,36,38-41]

$$\Delta G_{\text{ads}} = -RT \ln \frac{V_N P_{s,g}}{\pi_s m S} \quad (4)$$

where R is the gas constant, m is the mass of the catalyst in the column, and S is the specific surface area of the catalyst. According to the reported standard states, $p_{s,g}$ and π_s were considered as $101 \text{ kN}\cdot\text{m}^{-2}$ (1 atm) and $0.338 \text{ mN}\cdot\text{m}^{-1}$, respectively.

2.4.2. Enthalpy of adsorption

The heat of adsorption ΔH_{ads} can be calculated from the Gibbs-Helmoltz equation:

$$\frac{\partial(\Delta G_{\text{ads}}/T)}{\partial T} = -\frac{\Delta H_{\text{ads}}}{T^2} = -R \frac{d \ln V_N}{dT} \quad (5)$$

which can be rearranged to:

$$\Delta H_{\text{ads}} = -R \frac{\partial(\ln V_N)}{\partial(1/T)} \quad (6)$$

Adsorption enthalpies (ΔH_{ads}) can be obtained from the slope of plots of $\ln V_N$ versus $1/T$.

2.4.3. Standard surface free energy

The standard free energy of adsorption for polar solutes on solid surface includes contributions from both dispersive, $\Delta G_{\text{ads}}^{\text{d}}$, and specific interaction, $\Delta G_{\text{ads}}^{\text{s}}$ [41]. For n -alkanes, due to absence of specific interaction, $\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^{\text{d}}$, and the increment of adsorption energy for two successive alkanes, defined as the energy difference for the adsorption of the two alkanes (hexane/heptane, heptane/octane, etc.) [38], corresponds to the free energy of adsorption of a methylene group.

$$\Delta G_{\text{CH}_2} = -RT \ln \frac{V_{N(n)}}{V_{N(n+1)}} \quad (7)$$

where $V_{N(n)}$ and $V_{N(n+1)}$ are the retention volume of n -alkanes with (n) and $(n+1)$ carbon atoms, respectively.

The dispersive component of the surface energy (γ_s^{D}), intrinsic and nonspecific for all

molecules calculated by Dorris and Gray method [22,42], is due to London forces (Eq. 8).

$$\gamma_s^D = \frac{1}{4} \frac{\Delta G_{CH_2}^2}{\gamma_{CH_2} N^2 a_{CH_2}^2} \quad (8)$$

where N is the Avogadro number, a_{CH_2} is the cross sectional area occupied by a $-CH_2-$ group (0.06 nm^2), and γ_{CH_2} ($\text{mJ} \cdot \text{m}^{-2}$) is the surface tension of a surface consisting of CH_2 groups, which is directly related with the temperature according to the following equation [33,36,38].

$$\gamma_{CH_2} = 35.6 + 0.058(20 - T) \quad (9)$$

The specific component of the surface free energy is closely related to the parameter of specific interaction of polar solutes (I^{sp}) with the catalyst. This parameter involves the surface properties in terms of potential and acid-base interactions and can be determined from the difference of free energy of adsorption, $\Delta(\Delta G)$, between a polar probe and the real or assumed n -alkane with the same surface area, a_p [33,36,38]:

$$I^{sp} = \frac{\Delta(\Delta G)}{Na_p} \quad (10)$$

2.5 Dry reforming of CH_4 with CO_2

The dry reforming experiments at high temperature were carried out at atmospheric pressure in a conventional flow apparatus with quartz lining (i.d. = 3 mm). The stainless steel reactor was heated inside a furnace. Before reaction, 50 mg reduced catalyst (40-60 mesh) was activated in nitrogen at 1023 K for 3 h with a flow rate of $50 \text{ mL} \cdot \text{min}^{-1}$. CH_4 dry reforming with CO_2 was carried out at the desired temperature with a gas hourly space velocity (GHSV) of $60000 \text{ mL} \cdot \text{h}^{-1} \cdot \text{g}_{cat}^{-1}$ and a N_2 : CH_4 : CO_2 flow rate ratio of 3: 1: 1. The

effluent was analyzed using an on-line gas chromatography (GC-9160, Shanghai Ouhua Analysis Instrument Co. Ltd., China) with a thermal conductivity detector (TCD). H₂, CO, CH₄ and CO₂ were separated by a TDX-01 column containing carbon molecular sieve. The conversions of CH₄ and CO₂, the ratio of H₂/CO, and the turnover frequency of CH₄ (TOF_{CH4}) are defined as follows:

$$\text{Conv. of CH}_4 (\%) = \frac{(\text{CH}_4)_{\text{in}} - (\text{CH}_4)_{\text{out}}}{(\text{CH}_4)_{\text{in}}} \times 100 \quad (11)$$

$$\text{Conv. of CO}_2 (\%) = \frac{(\text{CO}_2)_{\text{in}} - (\text{CO}_2)_{\text{out}}}{(\text{CO}_2)_{\text{in}}} \times 100 \quad (12)$$

$$\text{H}_2/\text{CO} = \frac{(\text{H}_2)_{\text{out}}}{(\text{CO})_{\text{out}}} \quad (13)$$

$$\text{TOF}_{\text{CH}_4} = \frac{(\text{CH}_4)_{\text{in}} - (\text{CH}_4)_{\text{out}}}{60 \times 22400 \times m_{\text{Ni}}} \quad (14)$$

where (CO₂)_{in} and (CH₄)_{in} are the inlet flow rates of carbon dioxide and methane (mL · min⁻¹), (CO₂)_{out}, (CH₄)_{out}, (H₂)_{out}, and (CO)_{out} are the outlet flow rates of carbon dioxide, methane, hydrogen and carbon monoxide (mL · min⁻¹), and m_{Ni} is mole of Ni surface atoms.

3. Results and discussion

3.1 Catalyst characterization

The small-angle XRD patterns for KIT-6 and Ni/KIT-6 samples are shown in Fig. 2(a). The diffraction patterns of the series of Ni/KIT-6 samples were similar to that of KIT-6, suggesting that the structural integrity of the mesostructures were maintained after Ni modification. Wide angle XRD patterns (Fig. 2(b)) of KIT-6 and Ni/KIT-6 catalysts showed

broad peaks around 15-30° (2θ) due to the presence of amorphous silica [33,36]. At Ni loadings higher than 1.0 wt%, a peak appeared at 44.4° which was ascribed to the (111) diffraction of nickel crystals [43]. No nickel oxide diffraction pattern was found on the sample before IGC and dry reforming reaction tests, which was consistent with the TPR results that showed significant hydrogen consumption only for the sample without H₂/Ar reduction treatment (Fig. S2). This suggested that the impregnated nickel was completely reduced after H₂/Ar treatment at 773 K. The nickel particle size was around 3.8 nm and 6.8 nm for 1.0 wt% Ni/KIT-6 and 2.0 wt% Ni/KIT-6 using Scherrer's equation. However, the large error may occur due to the weak intensity. H₂-TPD showed that nickel dispersion decreased with increasing Ni loading (Table 1). At the low loading of 0.5 wt%, a high metal dispersion of 40.7% was achieved. The average particle size is less than 1.8 nm for 0.5 wt% Ni/KIT-6 according to the calculation based on the metal dispersion [6]. Thus, the formed species are small enough to locate inside the microporous channels.

TEM images (Fig. 3) of KIT-6 and Ni/KIT-6 samples showed an ordered gyroidal *Ia3d* mesostructure, which was the representative structure of KIT-6 materials [7,8]. No metal particles were detected for the 0.5 wt% loading sample, but some nanoparticles were observed on KIT-6 with Ni loadings $\geq$ 1.0 wt%. At the high Ni content of 2.0 wt%, nickel species began to aggregate and more large metal particles were detected outside the mesoporous channels (Fig. 3(d)). The average particle size around 5.5 nm was observed on 2.0 wt% Ni/KIT-6, which is similar with the calculation by the Scherrer's equation through XRD analysis (6.8 nm).

Fig. 4 shows the N₂ sorption isotherms of KIT-6 and Ni/KIT-6 catalysts. The isotherms

corresponded to type IV isotherm and showed a steep H1 hysteresis consequent of capillary condensation and evaporation at high-relative pressures (Fig. 4(a)), and is characteristic of materials with large pore sizes and narrow size distributions (Fig. 4(b)) [7,44,45]. BET specific surface areas, pore sizes and pore volumes of all samples are presented in Table 1. BET surface areas were between 686-728 m²/g for all samples, which were in line with literature values [7-9]. The surface areas, pore volumes and pore sizes decreased with Ni loading indicating that some blockage of KIT-6 channels had taken place. DFT model assuming a cylindrical pore geometry showed the complementary micropore size around 1.8 nm and main pore size around 10.0 nm (Fig. S3) for KIT-6 and Ni/KIT-6 samples, which was higher than the one calculated by the BJH method (Table 1). The micropore volume determined by t-plots [46] decreased greatly with the initial impregnation of 0.5 wt% Ni species, suggesting that the metal solution penetrated into the micropores preferentially. The preferential siting of Ni in the micropores might be related to the higher hydroxyl density of the inner pore surface which facilitated the penetration of the polar solution containing Ni species and capillary condensation effect. With more nickel loading, the pore volume decreased due to the blockage of large nickel particles detected on 2.0 wt% Ni/KIT-6 by TEM.

3.2. Inverse gas chromatography

3.2.1. Influence of the carrier gas flow rate on IGC measurements

In order that the IGC results reflected adsorption properties of the catalysts surface, the

measurements should be conducted free of diffusion influence, which could be tested by adjusting the carrier gas flow rates [31,33,36]. Fig. 5 shows that the net retention volume of *n*-alkanes was independent of the carrier gas flow rate over KIT-6 and Ni/KIT-6 at 473.2 K for carrier flow rates higher than 20 mL·min⁻¹. Thus, our measurements were performed under conditions that were not limited by external diffusion effects. Based on the data in Fig. 5, a flow rate of 28 mL·min⁻¹ was adopted to carry out the IGC measurements.

3.2.2. Free energy of adsorption

The standard free energies of adsorption were calculated using Eq. 3 and tabulated in Table 2. The adsorption energy, $-\Delta G_{ads}$, decreased with increasing temperature, in accordance with the van't Hoff equation for exothermic adsorption processes, and increased with the number of carbon atoms in the *n*-alkane molecule as expected. With nickel loading, the free adsorption energy decreased for *n*-alkane, trichloroethylene, tetrachloroethylene and cyclohexane due to the large loss of the micropore during the metal species impregnation (Table 1) [36]. When more nickel was impregnated, the free adsorption energy seemed to increase. But the error was so big that the increment can not be distinguished in Table 2. It was higher for the polar molecule trichloroethylene than tetrachloroethylene, suggesting its stronger interaction with the polar Si-O-H and Ni-O groups on the solid surface. It was also higher for aromatic compounds than cyclic and aliphatic hydrocarbons of the same carbon number. This phenomenon has been ascribed to the interaction between the solid and the aromatic ring as is shown in our recent work on MCF and Ni/MCF [33]. The weak acid sites of the hydroxyls of the silica [47,48] and the *d* orbitals of Ni can interact via acid-base

and $d-\pi$ interactions with the basic electron-rich π system of the aromatic ring [30,31,40]. Ni promotion was observed that the adsorption free energy for aromatic compounds were comparable on the 1.0 and 2.0 wt% Ni samples, which were higher than the similar values on the 0 and 0.5 wt% samples. The higher adsorption energy with 1.0 wt% than 0.5 wt% sample was also observed previously for Ni/MCF, a solid with no micropore [33]. These adsorption free energies were higher than those observed on many other mesoporous materials, such as $\gamma\text{-Al}_2\text{O}_3$ [49], KIT-6-1223 K [36] and $\text{SiO}_2\text{-H}$ [39], but similar to mesocellular silica foams materials MCF [33].

3.2.3. Enthalpy of adsorption

Enthalpies of adsorption $-\Delta H_{\text{ads}}$ were calculated using Eq. 5 from the slope of the plot of $R \ln V_N$ versus $1/T$ (Fig. S3), and the data are presented in Table 3. The adsorption enthalpies of n -alkanes increased with the carbon number due to increased van der Waals interaction [30,38,40]. On Ni/KIT-6 samples, trichloroethylene exhibited higher adsorption enthalpy than tetrachloroethylene, indicating that polar interaction was retained on the surface after Ni modification. ΔH_{ads} was more negative for benzene on Ni/KIT-6 than cyclic and aliphatic hydrocarbons with the same carbon number, i.e. cyclohexane and hexane. Similar to the free energy of adsorption ΔG_{ads} , the most negative ΔH_{ads} were found on the 1.0 and 2.0 wt% Ni/KIT-6 samples. With nickel loading, the largest enthalpy occurred on 1.0 wt% nickel loading sample. This phenomena could be explained by the large number of nickel species strongly contacted. However, except for benzene and toluene, the relatively large uncertainties in the enthalpy data made it difficult to discern the effect of Ni loading

on these samples.

3.2.4. Standard surface free energy.

The dispersive component of surface free energy, ΔG_{CH_2} may be determined from a plot of ΔG_{ads} versus the number of carbon atoms of the adsorbed *n*-alkanes. Based on Eq. 8, the dispersive interaction γ_s^D calculated for KIT-6 and Ni/KIT-6 samples at different temperatures are shown in Fig. 6. The γ_s^D value decreased with increasing temperature due to the entropic contribution ($-T(\Delta S_{CH_2})$) [30,36,39]. It was higher for KIT-6 containing ≥ 1.0 wt% Ni, when Ni particles began to form in the main mesopore as shown by XRD and TEM analysis. This dependence of the strength of dispersive interaction on the weight loading of metal had been reported before. The dispersive interaction on metal loading was reported for Rh/H-Beta [31] and mesoporous silica MCF modified by Ni in our recent work [33], where a 0.5 wt% sample exhibited higher dispersive interaction than 1.0 or 2.0 wt% samples. There are various contributing factors to the observed dispersive interaction: not only the quantity, accessibility, but also the nature of the metal surface, adsorbate and support surface. With higher Ni loading, the metal species tended to aggregate and form larger nanoparticles with less coordinately unsaturated sites on the surface (corners and edges), which could result in a weaker average weak dispersive interaction [50]. For our samples, the dispersive components (87, 98, and 94 $\text{mJ} \cdot \text{m}^{-2}$ at 463.2 K for 0.5, 1.0 and 2.0 wt%) did not vary proportionally with the relative quantity of exposed Ni surface atoms (estimated as weight loading times dispersion equaling, 20.4, 24.3, and 31.0%, respectively for the above three samples). Thus, other contributing factors must participate. The fact that

the dispersive interaction for the 1.0 and 2.0 wt% Ni/KIT-6 samples were comparable and higher than that of 0.5 wt% Ni/KIT-6 (Fig. 7), and the latter was comparable to KIT-6 without Ni. It was suggested that the less/weaker interaction of alkane occurred on Ni species with higher dispersion (smaller Ni particle size). The likely scenario was that some of these small Ni particles were not accessible to the probe molecule. This is consistent with our proposal of Ni preferential siting in the micropores at low loadings and the poor accessibility of these sites to probe molecules [36]. At higher metal loading (≥ 1.0 wt%), Ni particles began to populate the main channels of KIT-6 that are accessible to the probe molecules. Thus, an increase in the dispersive interaction was observed.

The specific interaction parameter, I^{SP} , was calculated using Eq. 10 from the $\Delta(\Delta G)$, which is the difference of adsorption free energy between the polar probes and *n*-alkane with same surface area. In order to estimate the adsorption free energy of alkanes with areas comparable to benzene, trichloroethylene, etc, the experimental ΔG_{ads} of alkanes were plotted against a_p , (Fig. 8), and ΔG_{ads} of other alkanes were estimated by extrapolation of this correlation. The specific interaction parameters thus obtained are shown in Table 4. Due to the occurrence of polar bridge oxygen atom on the solid surface, higher values of I^{SP} were found for the more polar trichloroethylene than for tetrachloroethylene. The values of I^{SP} for benzene were larger than for cyclohexane of the same carbon number on both KIT-6 and Ni/KIT-6. This is related to the interaction of the π -ring electrons with the acidic support hydroxyl groups [33,36,40] and with Ni [31,33].

The effect of Ni modification on the specific interaction of benzene is shown in Fig. S4. As a function of Ni loading, the specific interaction for benzene reached a maximum over

1.0 wt% Ni/KIT-6. This suggests that the specific interaction parameter is not dependent only on the amount of Ni but also on the nature and distribution of the Ni species in the different pore structures. Our recent study of benzene with Ni/MCF had shown that high I^{SP} occurred on highly dispersed Ni species [33]. Small metal particles are known to possess a high density of coordinatively unsaturated surface atoms which interact with aromatic ring strongly [6,50,51]. As the Ni particle size increases with increasing metal loading, this interaction becomes weaker due to agglomeration of Ni and concomitant loss of coordinately unsaturated sites [4,33]. This trend was clearly established previously for Ni/MCF with benzene and the interaction energies at 463.2 K were $80 \text{ mJ}\cdot\text{m}^{-2}$, $78 \text{ mJ}\cdot\text{m}^{-2}$ and $68 \text{ mJ}\cdot\text{m}^{-2}$ for 0.5, 1.0 and 2.0 wt% loadings, respectively [33]. However, this trend was not observed for Ni/KIT-6 (Fig. S4) which shows the maximum I^{SP} was at 1.0 wt% loading where Ni dispersion was 24.3%. As mentioned, at low loadings, Ni preferably resided in the micropore. Thus, the observation could be explained if these Ni particles in the micropores were not easily accessible to benzene. At 1.0 wt% Ni loading, the high I^{SP} was due to formation of Ni particles in the mesopores that were easily accessible by benzene. However, at an even higher loading (2.0 wt%), loss of coordinatively unsaturated sites consequent of agglomeration resulted in decline in specific interaction with the probe molecule (Fig. S4, Fig. 2(b) and Fig. 3(d)) [33,50,51].

Fig. 9. summarizes the interactions of benzene with a series of Ni/KIT-6 samples and compares them with similar loadings of Ni/MCF samples from our previous work [33]. The two supports differ in that only KIT-6 contains micropores. The maxima of both the dispersive and specific interactions of Ni/MCF sample occurred at 0.5 wt% when the Ni

particle size was the smallest and the metal particles possessed the highest number of coordinatively unsaturated sites. The maxima were displaced to 1.0 wt% Ni loading for the Ni/KIT-6 samples as Ni initially occupied the microporous sites and not all of the Ni was accessible [52]. Only at higher loadings, Ni populated the mesopores and were available to interact with benzene. At even higher loadings, the Ni particles on both supports agglomerated and hence the strongly interacting coordinatively unsaturated sites decreased proportionally, resulting in a decrease in the interaction with benzene.

3.3 Methane reforming with carbon dioxide

The surface property test by IGC shows Ni species may not play the role in the reaction when the active centers enter the micropore of KIT-6. A heterogeneous catalytic reaction of methane dry reforming was used to investigate the catalytic property of Ni/KIT-6 samples. Reforming of methane to valuable synthesis gas products is a green process and highly desirable [4,53-67]. Mesoporous silicas such as MCM-41, SBA-15, MCF and KIT-6 possess high surface area and thermal stability, which were used in the reforming catalysts synthesis [1,4,9,61,63-65]. Ni/SBA-15 was reported to be highly stable in the dry reforming reaction at 800 °C for 600 h without the obvious activity loss [1]. The catalytic activity of methane with carbon dioxide on Ni/KIT-6 is shown in Fig. 10. The conversions of methane and carbon dioxide increased with increasing reaction temperatures and there was no deactivation within 20 h of reaction tests. Enhancement of catalytic activity by Ni depended on metal loadings. The parent support was inactive and addition of 0.5 wt% resulted in methane and carbon dioxide conversions of 5.5% and 8.0% at 873 K, respectively. The

conversion of CO₂ was higher than CH₄ (Fig. 10(a)) and the H₂/CO ratio was 0.8, lower than unity (Fig. 10(b)). This could be attributed to the reverse water gas shift reaction, H₂ + CO₂ → H₂O + CO [4,65,66]. The reforming activity was higher for 1.0 wt% Ni sample, with a methane conversion of 12.0% at 873 K. The TOF_{CH₄} (moles of CH₄ reacted per mole of surface Ni per second, Eq. 14) increased with Ni loading up to 1.0 wt% Ni and then either declined slightly or remained the same within error at 2.0 wt% metal loading (Fig. 11). This increase in TOFs from 0.5 wt% to 1.0 wt% was unexpected, as the activity generally increased with decreasing metal particle size [50,51,65-67]. Our results could be explained using information derived from the IGC measurements. As mentioned earlier, we concluded from the IGC results that Ni first populated the ‘unaccessible’ micropores of KIT-6. Since the Ni particles (>2 nm according to dispersion measurements) were large enough to physically filled the micropores (average diameter 1.8 nm), only part of the Ni surfaces were accessible to the reactant molecules. The reaction kinetics of these Ni particles was also hindered by pore diffusion. At higher Ni loadings, the Ni also populated the mesopores where they were readily accessible to the reactants. Further increase in loading caused agglomeration of the Ni particles and decrease of the fraction of more coordinatively unsaturated sites and the TOFs.

According to the literatures [5,6,33,50,51,56,65-67], highly dispersed metal species can significantly promote the adsorption and activation of the reactants in the reaction due to their coordinately unsaturated metal sites. In smaller clusters rhodium surface atoms were found to activate C-H bonds more effectively than the larger one due to the occurrence of the coordinately unsaturated sites [51,65,66]. High TOF of benzene hydrogenation were

observed over Al_2O_3 loaded with small Ni particles (≤ 2 nm) [6]. The main contribution from highly dispersed species is the large occurrence of coordinately unsaturated metal sites such as the kinks, steps, and corners [50,51], on which the reactants can be adsorbed and interacted strongly [5,56]. This phenomenon also happens in surface property study by IGC [33]. Highly dispersed nickel species on MCF mesoporous silica can promote both the specific and dispersive interaction. However, all the supports used are uniform with the single dimension. For two dimension interconnecting structure such as meso-microporous silica [36,52], the microporous channel was partly penetrated into by the gas molecule and becomes ‘unaccessible’ by IGC evaluation. In this present work, IGC determination shows that highly dispersed Ni species entered the ‘unaccessible’ micropore of KIT-6 silica favorably, which decreased the efficiency of the active species in catalyzing the reactants in methane dry reforming with carbon dioxide.

4. Conclusions

Inverse gas chromatography at infinite dilution was successfully applied in evaluating the surface properties of KIT-6 modified with different amounts of Ni. The adsorption free energy, adsorption enthalpy, dispersive interaction, and specific interaction were obtained for KIT-6 and Ni/KIT-6 with IGC measurements. The dispersive and specific interaction were especially strong for aromatic probes. The maxima for adsorption free energy and adsorption enthalpy of aromatic probes for a series of Ni/KIT-6 samples occurred at 1.0 wt% Ni loading. The weaker interaction at 0.5 wt% was ascribed to preferential Ni occupancy of the micropores at the low metal loading where the Ni was not easily accessible to the probes. This model was supported by other physical characterization. Results from IGC measurements gave insight into the methane dry reforming reaction where the highest TOF_{CH_4} was not associated with the sample with Ni particles with the highest dispersion, again due to the fact that not all Ni surfaces were easily accessible for their preferential siting in the micropores at low Ni loadings.

Acknowledgments

This work was supported by the National Science Foundation for Fostering Talents in Basic Research of the National Science Foundation of China (J1103304), National Natural Science Foundation of China (61177021 and 21003024), Fudan's Undergraduate Research Opportunities Program (FDUROP) and Shanghai Science and Technology Committee (12DZ2275100).

Support Information

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Tables

Table 1 Texture properties of KIT-6 and Ni/KIT-6 samples

Sample	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_t ($\text{cm}^3 \cdot \text{g}^{-1}$) ^a	Pore Size	Micropore	Ni
			adsorption (nm)	Volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Dispersion (%)
KIT-6	728	0.76	7.5	0.075	---
0.5 wt% Ni /KIT-6	697	0.73	7.4	0.048	40.3
1.0 wt% Ni /KIT-6	692	0.70	7.3	0.046	24.7
2.0 wt% Ni /KIT-6	686	0.68	7.2	0.045	15.5

^a V_t total pore volume at relative pressure 0.99.

Table 2 Standard free energy of adsorption, $-\Delta G_{\text{ads}}$ ($\text{kJ}\cdot\text{mol}^{-1}$) for probes on the KIT-6 samples

Adsorbent/probe	Temperature (K)			
	463.2	473.2	483.2	493.2
KIT-6				
Hexane	9.06±0.06	8.63±0.13	8.15±0.14	7.58±0.10
Heptane	12.43±0.02	11.85±0.05	11.17±0.08	10.77±0.08
Octane	15.86±0.04	15.22±0.08	14.49±0.04	14.01±0.04
Nonane	19.14±0.05	18.58±0.05	17.68±0.07	17.25±0.05
Cyclohexane	9.96±0.12	9.36±0.06	8.75±0.14	8.20±0.08
Trichloroethylene	11.79±0.06	11.21±0.06	10.79±0.12	10.07±0.11
Tetrachloroethylene	9.84±0.10	9.22±0.14	8.79±0.08	8.15±0.07
Benzene	12.68±0.13	12.08±0.05	11.29±0.08	11.03±0.09
Toluene	16.55±0.11	15.82±0.09	15.27±0.11	15.08±0.04
0.5 wt% Ni/KIT-6				
Hexane	7.84±0.03	7.26±0.04	6.65±0.11	6.27±0.15
Heptane	11.54±0.03	10.94±0.02	10.36±0.05	9.87±0.06
Octane	14.48±0.01	13.73±0.03	13.15±0.02	12.58±0.03
Nonane	17.89±0.01	17.14±0.01	16.42±0.07	15.76±0.03
Cyclohexane	8.53±0.08	7.97±0.08	7.26±0.12	6.63±0.16
Trichloroethylene	11.27±0.02	10.82±0.05	10.12±0.08	9.68±0.10
Tetrachloroethylene	8.66±0.08	8.09±0.08	7.53±0.12	6.93±0.16
Benzene	12.68±0.09	11.94±0.04	11.33±0.05	10.65±0.07
Toluene	16.63±0.03	15.97±0.16	15.35±0.02	14.75±0.05
1.0 wt% Ni/KIT-6				
Hexane	7.96±0.11	7.47±0.15	6.94±0.17	6.27±0.33
Heptane	11.68±0.08	11.08±0.05	10.44±0.09	10.03±0.13
Octane	14.86±0.07	14.24±0.03	13.61±0.04	12.97±0.04
Nonane	18.91±0.08	18.26±0.11	17.58±0.08	16.73±0.02
Cyclohexane	9.50±0.11	8.81±0.12	8.14±0.19	7.56±0.33
Trichloroethylene	11.98±0.17	11.43±0.17	10.85±0.11	10.28±0.15
Tetrachloroethylene	9.68±0.10	9.17±0.12	8.66±0.19	7.91±0.33
Benzene	13.26±0.08	12.60±0.05	11.86±0.08	11.27±0.10
Toluene	17.28±0.11	16.52±0.03	15.94±0.04	15.36±0.07
2.0 wt% Ni/KIT-6				
Hexane	8.07±0.10	7.57±0.05	7.00±0.12	6.49±0.18
Heptane	11.73±0.03	10.99±0.05	10.67±0.05	10.00±0.07
Octane	15.19±0.04	14.47±0.02	13.91±0.02	13.19±0.06
Nonane	18.78±0.02	18.13±0.02	17.43±0.02	16.65±0.02
Cyclohexane	9.10±0.11	8.49±0.10	7.84±0.12	7.24±0.20
Trichloroethylene	11.88±0.05	11.43±0.05	10.83±0.06	10.23±0.08
Tetrachloroethylene	9.10±0.11	8.67±0.10	7.92±0.12	7.38±0.18
Benzene	13.20±0.03	12.48±0.03	11.82±0.14	11.18±0.06
Toluene	17.09±0.01	16.45±0.02	15.89±0.03	15.16±0.06

Table 3 Adsorption enthalpies $-\Delta H_{\text{ads}}$ (kJ·mol⁻¹) on KIT-6 samples

Probe	KIT-6	0.5 wt% Ni/KIT-6	1.0 wt% Ni/KIT-6	2.0 wt% Ni/KIT-6
Hexane	32.3±1.8	32.5±1.7	33.9±1.3	32.7±0.5
Heptane	38.7±2.0	37.4±0.9	37.5±1.6	37.2±2.7
Octane	45.0±1.9	43.6±1.5	44.1±0.2	45.6±1.1
Nonane	49.7±3.6	50.9±0.7	52.2±1.6	51.7±1.0
Cyclohexane	37.3±0.9	38.2±1.0	39.5±0.9	38.0±0.3
Trichloroethylene	37.6±2.2	36.6±1.7	39.2±0.3	37.6±1.3
Tetrachloroethylene	35.3±1.2	35.4±0.2	36.6±1.9	36.5±1.9
Benzene	39.3±3.4	43.6±0.8	44.5±1.0	44.3±0.6
Toluene	39.6±3.4	45.7±0.4	46.8±1.6	44.6±1.0

Table 4 I^{sp} (mJ·m⁻²) values determined on KIT-6 samples

Adsorbent/probe	Temperature (K)			
	463.2	473.2	483.2	493.2
KIT-6				
Cyclohexane	26.2±0.8	25.3±0.8	24.0±0.9	24.0±0.8
Trichloroethylene	68.0±0.5	66.7±0.9	65.1±0.9	64.5±0.9
Tetrachloroethylene	38.0±0.6	36.9±1.2	35.9±1.7	35.6±1.2
Benzene	74.3±0.8	72.9±1.0	69.2±0.8	71.1±1.0
Toluene	63.7±0.4	62.2±0.8	60.8±0.6	62.7±1.2
0.5 wt% Ni/KIT-6				
Cyclohexane	25.6±0.6	24.6±0.6	24.2±1.0	23.5±1.3
Trichloroethylene	72.6±0.8	71.2±0.8	69.9±1.1	68.5±1.5
Tetrachloroethylene	37.8±0.2	37.4±0.5	36.2±0.7	35.8±0.9
Benzene	79.3±0.9	77.2±0.4	76.6±0.5	73.5±0.7
Toluene	70.6±0.3	68.8±1.5	68.4±0.2	67.8±0.2
1.0 wt% Ni/KIT-6				
Cyclohexane	30.2±0.9	29.8±1.0	28.6±1.5	27.6±1.7
Trichloroethylene	80.3±0.9	78.5±1.5	76.6±1.7	75.4±2.2
Tetrachloroethylene	45.1±1.7	44.7±1.1	44.5±1.0	42.6±1.3
Benzene	88.0±0.7	84.4±0.4	82.6±0.7	82.4±0.9
Toluene	74.8±1.1	72.3±0.3	71.6±0.2	71.3±0.6
2.0 wt% Ni/KIT-6				
Cyclohexane	28.0±0.9	27.5±0.8	26.2±1.0	25.3±1.6
Trichloroethylene	76.1±1.0	76.8±1.0	75.0±1.1	73.2±0.7
Tetrachloroethylene	40.3±0.4	40.0±0.5	39.4±0.6	38.3±1.7
Benzene	85.5±0.3	84.0±0.3	81.9±1.3	79.9±0.6
Toluene	72.6±0.1	71.9±0.2	70.9±0.3	69.2±0.6

Figures

Fig. 1. Schematic drawing of structure of KIT-6 [7,8] and the Ni impregnation process.

Fig. 2. Small-angle (a) and wide-angle (b) X-ray diffraction patterns of KIT-6 and Ni/KIT-6 samples.

Fig. 3. TEM images of: (a), KIT-6; (b), 0.5 wt% Ni/KIT-6; (c), 1.0 wt% Ni/KIT-6; (d), 2.0 wt% Ni/KIT-6 (Ni nanoparticles were shown by the white arrows).

Fig. 4. Nitrogen sorption isotherms (a) and pore size distribution of adsorption according to the BJH method (b) for KIT-6 and Ni/KIT-6 samples.

Fig. 5. Effect of carrier gas flow rate on the retention volume at 473.2 K for hexane (■), heptane (●), octane (▼), nonane (▲) over KIT-6 (a) and 2.0 wt% Ni/KIT-6 (b).

Fig. 6. Dispersive interaction γ_S^D (mJ·m⁻²), of KIT-6 and Ni/KIT-6 samples as a function of the temperature.

Fig. 7. Dependence of dispersive interaction, γ_S^D (mJ·m⁻²), on nickel content of Ni/KIT-6 samples at the temperature: 463.2 K (▼) and 493.2 K (○).

Fig. 8. The dependence of adsorption free energy on a_p , over 0.5 wt% Ni/KIT-6 at 473.2 K.

Fig. 9. The dispersive interaction (a) and specific interaction of benzene (b) promoted by Ni modification on MCF [33] and KIT-6 samples (463 K and 493 K).

Fig. 10. The conversions of CH₄ and CO₂ (a) and the ratio of H₂/CO (b) on Ni/KIT-6 samples (GHSV= 60000 mL·h⁻¹·g_{cat}⁻¹).

Fig. 11. Turnover frequency of CH₄ (TOF_{CH₄}) on the KIT-6 modified by different content of Ni (873 K and 923 K, and GHSV = 60000 mL·h⁻¹·g_{cat}⁻¹).

Fig.1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.