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Mesoporous synthetic clays: synthesis, characterization, and use as HDS catalyst supports

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Mesoporous synthetic clays (MSCs) are obtained when polymer-containing silicate gels are hydrothermally crystallized to form layered magnesium silicate hectorite clays containing polymers that are incorporated in situ. Polyvinylpyrrolidone of several average molecular weights ranging from 10K to 1.3M, in gel loadings varying from 5-30 wt%, were used. The organic polymer template molecules were removed from synthetic polymer-clay complexes via calcination. Pore radii, surface areas, and pore volumes of the resulting porous inorganic networks were then measured. For the most part there is a direct correlation between both PVP molecular weight and polymer loading on the diameter of the average pore. In addition to conventional techniques, the polymer-clay materials were also characterized by small angle x-ray scattering to ascertain the disposition of the polymeric matrix. The MSC materials after calcination were examined as potential supports for hydrodesulfurization (HDS). They were loaded with a bimetallic Co/Mo catalyst system for comparison with a commercial Co/Mo alumina catalyst. Dibenzothiophene (DBT) diluted with hexadecane (0.75 wt% S) was utilized as a liquid feed for the HDS tests. This feed was chosen as a deep HDS test of a heavy model oil. The pore diameters of the MSC catalysts were found to have a strong effect on both the HDS activity and selectivity.

1. INTRODUCTION

Recently we reported the synthesis of mesoporous synthetic clays (MSCs) derived from polymer-containing silicate clay gels [1]. In this in situ technique, interlayer intercalation of different polymers over broad molecular weight and concentration ranges is achieved. At the same time, small stacks of clay layers (tactoids) are themselves imbedded randomly in a polymer matrix. While individual interlayer spaces collapse due to loss of template upon calcination, a stable and intact pore system results from removal of template that existed between tactoids. Polyvinylpyrrolidone (PVP) was used as a template of pore size of these magnesium silicate layered clays, which occurs in the mesoporous range of 40-100 Å. Here we report our efforts on: (a) expanding this pore size range, (b) further characterization of the polymer-clays by small angle x-ray scattering, and (c) the use of the MSCs as catalyst supports in preliminary hydrodesulfurization catalytic testing.

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2. EXPERIMENTAL

2.1 Clay Synthesis and Characterization

The typical method for in situ hydrothermal crystallization of the polymer-hectorite clays is to create a 2 wt% gel of silica sol, magnesium hydroxide sol, lithium fluoride, and polymer in water, and to reflux for 2 days. Complete details can be found elsewhere [1]. Most chemical reagents were purchased from Aldrich. Polyvinyl pyrrolidones were provided with average M_w values of 10K, 29K, 55K, and 1.3M, and a PVP of M_w 360K was obtained from Sigma. Polymers were added at the 5-30% by weight loading of the total gel solids components. For example, when 2 gms gel solids (SiO_2 , $\text{Mg}(\text{OH})_2$, LiF) are dispersed in 200 ml H_2O , 0.50 gm polymer are added ($0.5/2.5 \times 100 = 20\%$). This mixture is refluxed for 48 hours then centrifuged and the products are washed and air-dried. Calcinations are carried out in a tube furnace using quartz tubes and boats at 500°C for 12 hr in air. In a few cases where excessive amounts of carbonaceous deposits remained, conditions were raised to 550°C for 12+ hrs in O_2 .

XRD analyses were carried out on a Rigaku Miniflex+ instrument using Cu K_α radiation, a NaI detector, variable slits, a 0.05° step size, and a 0.50° $2\theta/\text{min}$ scan rate. Powders were loosely packed in horizontally held trays. TGA-DTA (thermal gravimetric analysis and differential thermal analysis) measurements were obtained on a SDT 2960 from TA Instruments. For these samples, measured against an alumina standard in a 100 ml/min O_2 flow with a temperature ramp of $10^\circ\text{C}/\text{min}$ to 800°C , no major differences were observed between TGA and DTA. Total polymer loadings were calculated by measuring the weight loss over the approximate temperature range of 200 - 600°C . Nitrogen adsorption and desorption isotherms were collected on either an Autosorb-6 from Quantachrome or a Micromeritics ASAP 2010. Approximately 0.10 gm of material was weighed into a pyrex sample tube and evacuated to 80 mTorr overnight at room temperature, then backfilled with He. The static physisorption experiments measured the amount of nitrogen adsorbed or desorbed as a function of pressure ($P/P_0 = 0.025$ -0.999, increments of 0.025). Pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) method. The desorption isotherm is normally used as a basis for the calculation of pore size distributions, although an artifact at 38 Å that occurs for all layered materials [2] also was observed for all of our clay samples. Pore radii were therefore determined from visual inspection of the curves, ignoring the artifact. Desorption pore volumes are reported; adsorption pore volumes were either the same or only slightly lower.

2.2. Small Angle X-ray Scattering (SAXS)

The SAXS instrument was constructed at ANL and used on the Basic Energy Sciences Synchrotron Radiation Center CAT undulator beamline ID-12 at the Advanced Photon Source [3]. Scotch tape was used to hold the clay samples. SAXS data were collected in 5 min scans. Monochromatic X-rays at 10.0 keV were scattered off the sample and collected on a 19×19 cm^2 position sensitive two-dimensional gas detector. The scattered intensity has been corrected for absorption, blank scotch tape scattering, and instrument background. The differential scattering cross section can be expressed as a function of the scattering vector Q , which is defined as: $Q = 4\pi (\sin \theta)/\lambda$, where λ is the wavelength of the X-rays and θ is the scattering half angle. The value of Q is proportional to the inverse of the length scale ($\text{\AA}^{-1}$). The instrument was operated at a sample-to-detector distance of 68.5 cm to obtain data at $0.04 < Q < 0.7 \text{ \AA}^{-1}$. Mylar windows were used because it does not have diffraction peaks in this Q range.

2.3. Catalyst Preparation

Aqueous ammonium heptamolybdate (Alfa, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 99.999%) solutions were prepared so that a metal loading of 6 wt % Mo would fill 80% of the available pore volume of the mesoporous synthetic clays. Following Mo impregnation and recalcination using the aforementioned conditions, the pore volumes were measured again using an established LN_2

physisorption protocol. Aqueous cobalt nitrate (Alfa, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.999%) was impregnated onto the calcined Mo/clay materials so as to provide a 2 wt % Co loading spread out over 80-85% of the remaining pore volume.

2.4. Catalytic Hydrodesulfurization (HDS) Testing

The catalyst pretreatment process for both the clay-supported and the reference catalysts consists of loading into the HDS reactor under N_2 , purging in N_2 at 20°C for 30 minutes at 1000 cm^3/min ., drying in N_2 at 150°C for 60 minutes and at 400°C for 60 minutes, and finally sulfiding in a 5% $\text{H}_2\text{S}/\text{H}_2$ mixture at 400°C for two hours prior to use as catalysts. The laboratory scale liquid-phase continuous-flow HDS reactor consists of a thick-walled 0.375" ID 316 SS tube, with 1 gm catalyst diluted with 5 gm tabular alumina (LaRoche T-1061, 10 m^2/gm) sitting between plugs of quartz wool. Beneath the lower plug is a 0.125" ID, 0.375" OD deadman used to minimize volume between the reactor and the liquid receiver. The liquid test feed consisted of 0.75 wt % sulfur as dibenzothiophene (DBT), dissolved in hexadecane and is representative of a middle distillate oil. All liquid-filled lines were heated to 50°C. The reaction was carried out at 400°C; LHSV = 10-40/h.

The products were diluted with hexane (1 mg product / 200 ml hexane), separated using a DB5-MS column, and analyzed using an HP 5890 GC-MS Series II Plus. Random errors associated with GC-MS concentration measurements were less than 5%, and the reproducibility of conversion measurements was $\pm 15\%$ of the reported values. Selectivity is defined as the percentage of biphenyl (the preferred HDS product from dibenzothiophene) divided by the percentage of dibenzothiophene converted times 100.

3. RESULTS AND DISCUSSION

3.1. SAXS results

Polyvinylpyrrolidone (PVP)-hectorite clays made via this synthetic method have been characterized exhaustively by XRD and TGA [1,4] prior to their calcination. Basal spacings in many cases were either weak or unobservable. In those cases two possibilities are responsible: either the basal spacings are too high and therefore out of detectable range of the XRD instrument, or the samples have delaminated. In order to obtain a thorough understanding of the composite materials prior to calcination, it was deemed necessary to ascertain which of these two scenarios was responsible. Small angle x-ray scattering (SAXS) was carried out for this purpose, and Figure 1 shows an example of the SAXS data. The curves in this figure correspond to PVP-hectorites made at the 30 wt% loading level, where XRD basal spacings range from 24.5 Å to non-existent. Two peaks are observed before the detector begins to fade ($>0.7q$) that correspond to about 24 Å ($.26 \text{ Å}^{-1}$) and 9.9 Å ($.63 \text{ Å}^{-1}$), where $q = 2\pi/d$. The former peak is obviously the basal spacing, while the latter peak is due to scattering from single clay sheets. Note the weakness of the basal spacing for the 360K and 1.3M PVP samples, as they are in XRD. But the critical factor is that no other peaks are seen. This combined with the weak intensities is evidence that the materials become delaminated (exfoliated) rather than simply swollen from more and more polymer incorporation. These scans cover the q -range out to $.04 \text{ Å}^{-1}$, equivalent to 157 Å, which is more than enough to see a swelling phenomenon. SAXS data for samples made at the 10% and 20% PVP loadings were also consistent with these conclusions.

3.2. MSC pore system and stability

Previously we reported the synthesis of MSCs derived from PVP-clays with resulting pore sizes as demonstrated in Figure 2 [1]. From this figure, one can see that pore size is dependent upon both the molecular weight and the wt% loading of polymer in the gel. The most sensitive results with respect to molecular weight occur at the lower loadings, as Figure 2 shows for 10 wt%. The smaller molecular weights (10-55K) span the lower pore size range

Figure 1. SAXS high-q data for 30 wt% synthetic PVP-hectorites (prior to calcination).

Figure 2. A correlation plot for pore size of PVP MSCs based on polymer wt% and M_w (in legend). A target pore of 70 Å diameter is demonstrated as derived from a 16 wt% 1.3M PVP-hectorite.

of 40-60 Å, and the larger molecular weights (360K-1.3M) cover approximately the 60-90 Å range. As loadings increase to 20-30 wt%, it is obvious that the sensitivity to pore size is markedly decreased. It is possible that this is due to the increased difficulty in removing larger amounts of polymer completely by calcination, and the more rigorous conditions that are required to do so.

In any event, considering this sensitivity to lower loadings, data at the 5 wt% loading level was desired in the hopes that an even greater pore size range could be achieved. Samples were prepared, characterized by XRD and TGA (see Table 1), calcined, and further characterized by nitrogen sorption experiments. The results, however, show pore size distribution (p.s.d.) behavior that is a bit different from expected. The actual p.s.d. data is shown in Figure 3. The lowest M_w 's of 10K and 29K do not have a definite peak in the dV/dD plots of the mesoporous region (ignoring the 38 Å artifact [2]), but there is however some pore volume present. The other three samples derived from 55K, 360K, and 1.3M PVP have pore diameters of 52 Å, 70 Å, and 70 Å, respectively. Therefore, decreasing the loading to 5% from 10% did not create larger pores.

The most productive way to use Figure 2, which demonstrates the power of this in situ synthetic technique, is to identify a target pore size and determine the exact polymer M_w and wt% loading required for its creation. An example of this is indicated by the solid lines in the figure for a target pore size of 70 Å. When a 16 wt% loading of 1.3M PVP is used to create this tailored MSC, the actual pore size was measured at 77 Å. This is an acceptably close value considering that the line connecting the 1.3M data is somewhat arbitrary at this stage (as more samples are made this line will of course become more predictive).

The stability of the MSC pore system is subject to some change as time passes after calcination. Table 2 shows the comparison of nitrogen sorption data from fresh samples and those 1.3 years old. The changes range from minor (12-22% loss in surface area, small differences in pore volumes and p.s.d.'s) to drastic (50% loss in surface area, large increases in p.s.d.). It has been proposed that the structure of the open network might be one based on interlocking tactoids [5], and it certainly possible that this structure would collapse somewhat with time.

Table 1
Characteristics of synthetic PVP-hectorites*

PVP gel wt% PVP	loading (wt%) by TGA	basal spacing, Å	BET S.A. m ² /gm calcined	desorption pore volume, cc/gm, calcined
5	3.4-6.6	16.8-17.7 weak	235-272	.53-.59
10	8.6-9.3	17.3-33.5 weak	226-251	.37-.54
20	13.6-16.0	17.5-18.4, none at high M_w	217-258	.37-.44
30	17.9-20.7	24.5-25.6, none at high M_w	227-249	.39-.41

*range of data presented for all five molecular weight samples from 29K to 1.3M.

Figure 3. Pore size distributions from N_2 desorption isotherms of synthetic PVP-hectorite MSCs made from 5 wt% loadings of PVP polymer at M_w 's of: (a) 10K, (b) 29K, (c) 55K, (d) 360K and (e) 1.3M.

Table 2
Stability of MSC pore system with time*

MSC polymer	<u>directly after calcination</u>			<u>1.3 years after calcination</u>		
	S.A., m ² /g	P.D., Å	P.V., cc/g	S.A., m ² /g	P.D., Å	P.V., cc/g
10% 10K	250	41.8	.37	202	41.5	.32
10% 29K	250	42.0	.37	209	53.9	.38
10% 55K	226	50.6	.40	199	55.2	.36
10% 360K	233	74.0	.46	184	76.0	.48
10% 1.3M	227	90.6	.54	126	70.0	.45
20% 10K	250	42.0	.37	135	broad	.28
20% 29K	237	54.4	.41	189	53.0	.36
20% 55K	217	58.4	.41	68	65, 120	.25
20% 1.3M	258	62.8	.50	136	73.2	.37
30% 29K	242	50.6	.41	200	53.9	.37

*S.A. = surface area, P.D. = pore diameter, P.V. = pore volume

3.3. HDS catalysis

Dibenzothiophene (DBT) diluted with hexadecane (0.75 wt% S) was the liquid feed for HDS tests. The pore diameter of the MSC catalysts is seen to have a strong effect on both the HDS activity and selectivity (Figure 4). In a previous study [6], two synthetic hectorites were compared using the same conditions as reported here except that a 1 wt% S feed was utilized. The samples were a control synthetic hectorite made without template, which contains micropores only, and one made with tetraethylammonium ions which had a pore diameter of 62 Å. The DBT conversion and BP selectivity were 3 times and 1.3 times higher, respectively, for the mesoporous material.

For the PVP-MSC catalysts, an increasing pore diameter leads to a nearly linear increase of activity along with an exponential boost in selectivity to biphenyl, and there is little indication that either parameter is leveling off at 90 Å. This means that larger pores are likely to give higher conversions and selectivities. The dependence on pore size may have many reasons, among them: (1) the internal diffusion of large molecules such as DBT may play a critical role in the HDS reaction, and (2) the size and disposition of the Co/Mo clusters, which would likely be quite dependent upon the pore size into which they are loaded. Higher selectivities were achieved in larger pores possibly because they make it easier for biphenyl molecules to diffuse out and prevent them from further hydrogenation and hydrocracking. Certainly the results show a definite dependence on pore size in the mesoporous range and warrant further exploration.

Figure 4. Hydrodesulfurization reactivity of dibenzothiophene using Co/Mo MSC catalysts.

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