

TECHNIQUE OF PREPARING MODIFIED SILICA FROM OIL SHALE RESIDUE

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The raw material – residue of oil production from Huadian oil shale – was modified with cationic surfactants; the hydroxyl groups on the aggregated silica surface were alkylated directly. The structure of alkylated Si-hydroxyl on modified silica surface was characterized by means of infrared spectroscopy, nuclear magnetic resonance analysis, thermal gravimetric analysis and scanning electron microscopy analysis. The results showed that modification rate of hydroxyl groups on the surface of the modified silica obtained was about 84%. The modification conditions were optimized basing on application of the orthogonal experimental method, and the optimum parameters were as follows: the reaction temperature of water medium – 40 °C, pH value within the range of 9–10, and the molar ratio of cationic surfactant to silica hydroxyl on the surface – 2:1.

INTRODUCTION

China is one of the countries that possess rich reserves of oil shale. Proven reserves of 50 billion tonnes are mainly distributed in Huadian and Nongan (Jilin province), Maoming (Guangdong province), Fushun (Liaoning province) and so on [1]. The investigation of mineral composition of each oil shale has shown that organic matter content of oil shales is low (usually less than 35%), while quartz, muscovite, kaolinite and calcite are the dominating minerals [2]. So making use of oil shale to produce shale oil or burning directly for power supply could produce large amounts of residue or ash, for example, if 600,000 tonnes of shale oil are produced per year, nearly 7 million tonnes of oil shale residue are formed. SiO₂ content of oil shale residue is the largest (approximately 50% or more), followed by Al and Ca. Synthesis of Ca-Al-Si-hydrates from oil shale ash with alkali treatment, for

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producing adsorbents, zeolite and molecular sieve is one of the methods of comprehensive utilization of oil shale [3–5]. Making silica from the oil shale residue is the second method of comprehensive utilization of oil shale [6–13]. Silica may be used as thickening agent of rubber and strengthening agent of coating products. The residue is neither able to react, nor compatible with organics, difficult to infiltrate and disperse because of hydroxyls on its surface, so hydroxyls must be alkylated to get hydrophobic modified silica [14–21]. Modified silica can be obtained from the oil shale residue by treating it with silane coupling agents vinyltrimethoxysilane (AH-171) and N-(normal-butyl)-3-aminopropyl trimethoxysilane (DYNASYLAN 1189) as modifiers, and adopting the process route of calcination and activation → alkaline dissolution → homogeneous sedimentation with ethyl acetate → modification with silane coupling agents, at what the modification rate of hydroxyls on the surface are 93.7% and 71.2% [21], respectively. The process of using silane coupling agents requires a lot of expensive ethanol as solvent, and a cheap modification technology would be more conducive to high-value reuse of the oil shale residue. This paper reports on the modified preparation of silica from oil shale residue by using cationic surfactant as modifier and water as reaction medium. Structural characteristics of the modified silica were analyzed.

Experimental

Sample

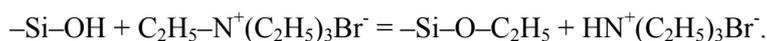
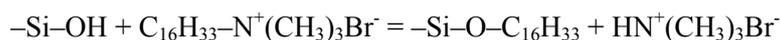
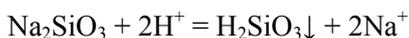
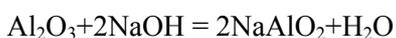
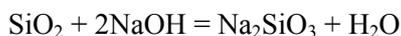
The residue (semicoke) was formed at pyrolysis of Huadian oil shale in the temperature range of 510–650 °C in the process of producing shale oil by means of the solid heat-carrier method. The inorganic composition of the residue formed is shown in Table 1. The samples were pretreated by calcination at 800 °C.

Table 1. XRF analysis of semicoke of Huadian oil shale (inorganic composition)

Component	Content, wt.%	Component	Content, wt.%
SiO ₂	54.3	P ₂ O ₅	0.158
Al ₂ O ₃	18.6	SrO	0.0917
CaO	9.16	CuO	0.0618
Fe ₂ O ₃	8.55	Cr ₂ O ₃	0.0532
SO ₃	3.16	MnO	0.0466
MgO	2.54	NiO	0.0251
K ₂ O	1.74	ZrO	0.0228
Na ₂ O	0.794	CoO	0.0156
TiO ₂	0.685		

Principle and method of preparation

Clay minerals are the dominant mineral components of oil shale residue, which do not react with acid and alkali due to the lack of chemical activity, but they can be converted into active compounds by calcinating, the active compounds react with NaOH solution at a certain temperature and SiO₂ and Al₂O₃ are transformed into Na₂SiO₃ and NaAlO₂, soluble in filtrate. Na₂SiO₃ can further be transformed into precipitate of hydrated silica (silica) and be separated from the filtrate, while aluminium still remains in the form of NaAlO₂ in the filtrate after adjusting the filtrate pH value between 8 and 9. Modified silica can be obtained by using cationic surfactants (hexadecyl trimethyl ammonium bromide and tetraethylammonium bromide). The reaction formulas are as follows:



The oil shale residue from oil production was comminuted to the size about 0.2 mm, a certain amount of it was put into the crucible, calcined and activated in a temperature range of 700–800 °C for 1.5 h in a muffle furnace. After cooling down the activated residue was taken out and loaded into a round-bottom flask, into which the solution of 25% NaOH was added at the liquid-solid ratio of 4:1. The mixture reacted at constant temperature of 40 °C for 2 h under magnetic stirring (pH = 12–13). Hot solution was filtered, ethyl acetate was added as acidifier, and H₂SiO₃ was precipitated at a constant temperature in a water bath (40 °C) under magnetic stirring. After precipitation it was separated centrifugally and washed by ethanol and deionized water. Precipitated silica was dissolved in water at liquid-solid ratio of 3:1, the mixture of alkali solution (NaOH:Na₂CO₃ = 1:1) was added and pH value was adjusted to 9–10 under stirring for 3–5 min. A certain amount of cetyl tri-methyl ammonium bromide and 4-ethyl bromide (pre-dissolved in water at 40 °C) was added into the system under stirring, and let to react at a constant temperature between 30–40 °C for 2 h until pH value reached a constant value between 8 and 12. After the mixture was centrifugally separated and washed with water (40 °C) to remove the non-reacted surfactant, the product was dried for 2 h by infrared light. Two kinds of silica modified by cationic surfactants were obtained. The infrared spectrometer (Nicolet AVATAR 370), NMR spectrometer (Varian Mercury Plus 400), scanning electron microscope (HITACHI S-4800) and thermogravimetric analyzer (TG209C) were applied to analyze the product.

Modification experiment

Modification conditions include: the dosage of cationic surfactants (the molar ratio of surfactant to hydroxyl number N on the sediment silica surface), reaction temperature, and pH value of the reaction system. In order to get a higher rate of modification, the orthogonal experiment $L_9(3^3)$ conditions (shown in Table 2) were used. Silica obtained according to the method given above was modified in different conditions to investigate the influence of different conditions on the modification effect (represented by the difference ΔN between the number of hydroxyls on the surface before and after the modification). The number N of hydroxyls per square meter of the surface of silica is calculated according to the following equation (number/nm²) [21]:

$$N = \frac{CVN_A \times 10^{-3}}{Sm},$$

where: C – concentration of sodium hydroxide solution (0.1 mol/L);
 V – the volume of 0.1 mol/L NaOH solution (pH ranges from 4.0 to 9.0), L;
 N_A – Avogadro konstant;
 m – sample mass, g;
 S – specific surface area, m²/g.

Table 2. Orthogonal experimental conditions $L_9(3^3)$

Modifier dosage	Reaction temperature, °C	pH value
1:1	30	8–9
2:1	35	9–10
3:1	40	10–12

Product analysis

The methods of analysis listed above were applied to analyze two kinds of silica modified with cationic surfactants. The modification effect was analyzed by comparing the results measured for the unmodified and modified silica.

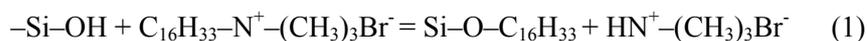
Results and discussion

Optimization of modified silica preparation from oil shale residue

The oil shale residue formed in the process of oil production was modified with hexadecyl trimethyl ammonium bromide applying the method of orthogonal experiments varying the amount of surfactant (the molar ratio of the cationic surfactant to the hydroxyl group number N of the silica surface),

reaction temperature and pH value of the reaction system. The corresponding changes in hydroxyl number (ΔN) of the modified silica surface are given in Table 3. As seen in Table 3, we determine the main factor basing on the R_j values determined for each factor, so the order of influencing factors in this experiment is $B > C > A$, what means that the greatest influencing factor in the modification reaction is reaction temperature, followed by pH value of the system, and the amount of modifier. By selecting the maximum from the sum of ΔN corresponding to I_j , II_j , III_j the optimum reaction conditions are B_3 , C_2 , A_2 : reaction temperature 40 °C, pH value within the range of 9–10, modifier dosage (the molar ratio of cationic surfactant to silica surface hydroxyl) 2:1. Using hexadecyl trimethyl ammonium bromide and tetraethylammonium bromide as modifiers, products with high rate of modification were obtained. The reactions occur according to the reactions (1) and (2). The modification results are shown in Table 4.

hexadecyl trimethyl ammonium bromide-modified:



tetraethylammonium bromide-modified:



One can see in Table 4 that the rates of modification with both hexadecyl trimethyl ammonium bromide and tetraethylammonium bromide are about 84%. The effect of the surface structure of silica is shown in Fig. 1.

Table 3. The results of orthogonal experiment, modifier – hexadecyl trimethyl ammonium bromide

Experiment number	Factor	Modifier dosage	Reaction temperature, °C	pH value	ΔN
1		1:1	30	8–9	2.67
2		1:1	35	9–10	3.75
3		1:1	40	10–12	3.93
4		2:1	30	9–10	4.09
5		2:1	35	10–12	3.87
6		2:1	40	8–9	4.39
7		3:1	30	10–12	3.67
8		3:1	35	8–9	2.95
9		3:1	40	9–10	4.43
I_j		10.35	10.43	10.01	
II_j		12.35	10.57	12.27	
III_j		11.05	12.75	11.47	
R_j		2.00	2.32	2.26	
Optimum level		A_2	B_3	C_2	
Factors' order	$B > C > A$				

Note: 1) I_j , II_j , III_j – the sum of three experiment results ΔN correspond to three levels.

2) R_j – Differences between maximum and minimum values of I_j , II_j and III_j .

Table 4. Modification with cationic surfactants

Item	Non-modified	Cationic surfactant	
		Hexadecyltrimethylammonium bromide	Tetraethylammonium bromide
N_{OH} (number/nm ²)	5.66	0.89	0.87
ΔN_{OH} (number/nm ²)		4.77	4.79
Modified rate, %		84.2	84.6

Modification rate can be to a certain extent affected by three kinds of hydroxyl position on the surface (isolated hydroxyl, ortho-dihydroxy and double hydroxyl) because of the hydrogen bond association in ortho-dihydroxy and steric hindrance of double hydroxyl.

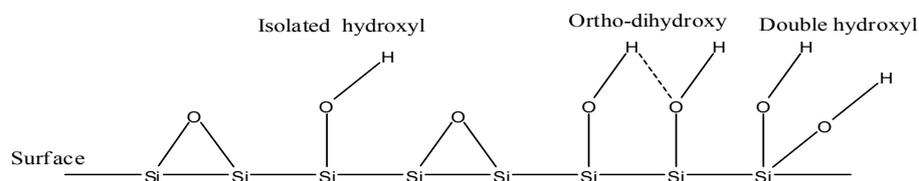


Fig. 1. Surface structure of silica.

Structure analysis of modified silica obtained from oil shale residue

Two kinds of modified silica obtained from oil shale residue by taking hexadecyl trimethyl ammonium bromide and tetraethylammonium bromide as modifier, respectively, were analyzed by infrared spectra. The results are shown in Fig. 2. Comparison with the infrared spectrum of unmodified silica in Fig. 3 shows that the intensity of hydroxyl stretching vibration peak at 3422.94 cm^{-1} is decreased after modification due to the reduction of hydroxyl number on the surface. However, hydroxyl has not completely reacted (the modification rate was 84%), so there are about 16% of the surface hydroxyl still unconverted. Two new stretching vibration peaks of C–H bond at 2920 cm^{-1} and 2850 cm^{-1} after modification indicate that the characteristic structure of Si-hydroxyl has been alkylated.

The ¹H NMR analysis results of two kinds modified silica are given in Table 5. There is a group of hydrogen peaks of Si-hydroxyl of unmodified silica in the high-field region (chemical shift within the range of 1.0–1.5 ppm), triplet hydrogen peaks corresponding to three kinds of Si–OH – isolated hydroxyl, ortho-dihydroxy and double hydroxyl. New peaks of hydrogen in the high-field NMR spectra of the modified silica belong to the hydrogen of silane chain $-\text{C}_{16}\text{H}_{33}$ and $-\text{C}_2\text{H}_5$. It demonstrates that the characteristic structure of Si-hydroxyl on the surface has been alkylated.

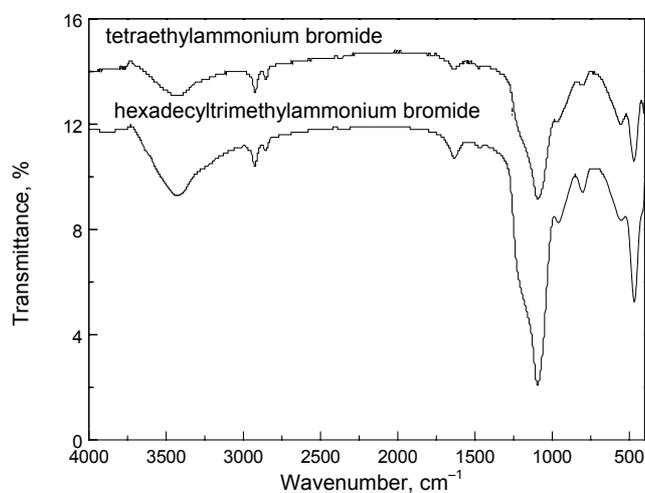


Fig. 2. IR spectrogram of silica modified with cationic surfactant.

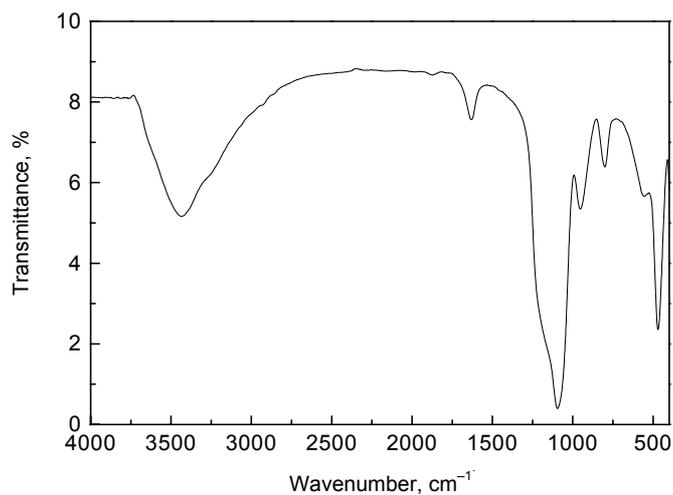


Fig. 3. IR spectrogram of unmodified silica.

Table 5. Results of nuclear magnetic resonance analysis

Samples	H chemical shift δ , ppm	The number of split peaks	H assignment
Unmodified silica	1.0–1.5	triplet	–OH
Hexadecyltrimethyl ammonium bromide-modified	2.2–1.9	multiplet	–C ₁₆ H ₃₃
Tetraethylammonium bromide-modified	2.1–1.7	triplet, quartet	–C ₂ H ₅

Two kinds of modified silica were analyzed also by thermal gravimetric method, and the results are shown in Figures 4 and 5 including that of the unmodified silica. As seen in Fig. 4, there are two obvious weight loss stages during the heating process of the modified silica. The first loss occurs from room temperature to about 150 °C due to water absorbed by the surface. The other obvious weight loss (about 4–4.5%) from 250 °C to 400 °C corresponds to the fracture of the alkyl chain of siloxane. This demonstrates the formation of a new valence-bond of $-\text{Si}-\text{OR}$ grafted on to alkyl chains in the modified silica.

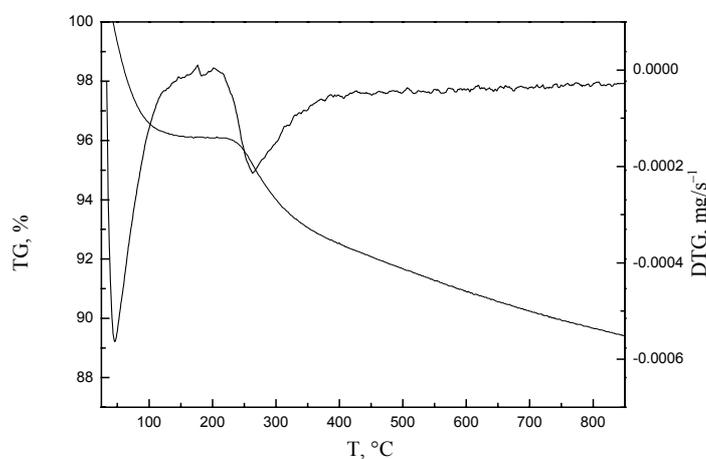


Fig. 4. TGA curve of modified silica.

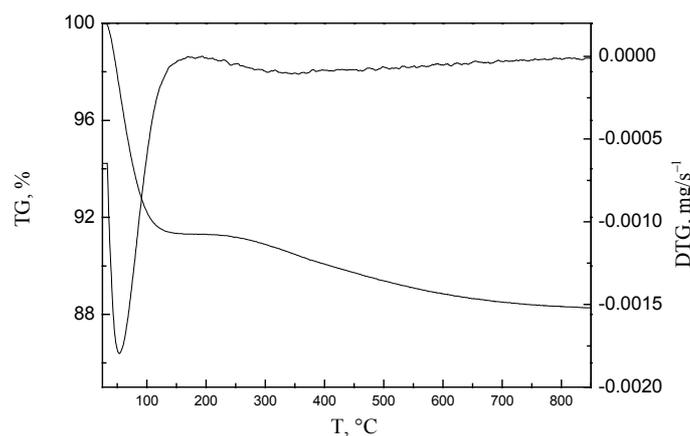


Fig. 5. TGA curve of unmodified silica.

Figures 6–8 are scanning electron micrographs of unmodified silica and modified silica. The conglomeration degree of modified silica particles is significantly reduced, especially when using hexadecyl trimethyl ammonium bromide. The dispersed particles are spherical and uniform-sized because the association between the original hydroxyls was impossible for introduction of alkyl chains, and agglomeration was greatly inhibited. As the C_{16} alkyl chains are longer than the ethyl chains, the modification effect is greater.

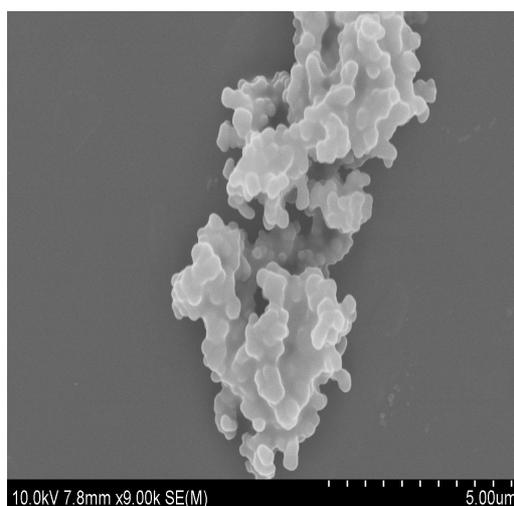


Fig. 6. SEM picture of unmodified silica.

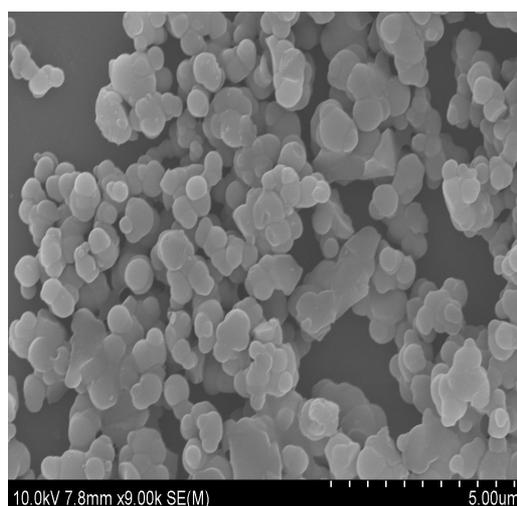


Fig. 7. SEM picture of silica modified with hexadecyl trimethyl ammonium bromide.

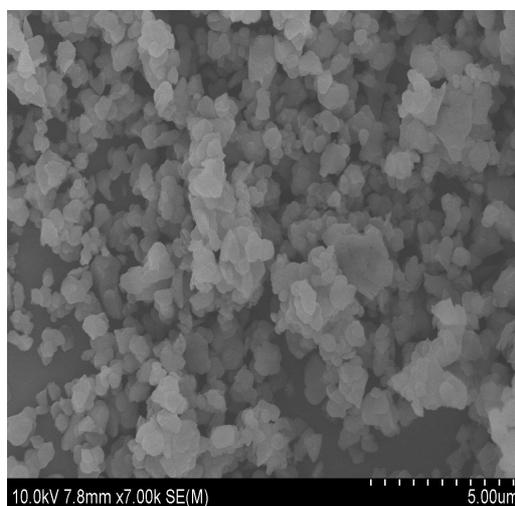


Fig. 8. SEM picture of silica modified with tetraethylammonium bromide.

Conclusions

Modified silica with high modification rate (84%) was obtained from oil shale residue by using cationic surfactants hexadecyl trimethyl ammonium bromide and tetraethylammonium bromide as modifiers. Optimum reaction conditions were determined by the orthogonal experimental method. The optimum conditions are: the reaction temperature of the water medium 40 °C, pH value between 9 and 10, the molar ratio of cationic surfactant to silica surface hydroxyl 2:1. The structure of the alkylated Si-hydroxyl on the silica surface was investigated by infrared spectroscopy, nuclear magnetic resonance analysis and thermal gravimetric analysis. The results indicate that a new valence-bond of $-\text{Si}-\text{OR}$ grafted with alkyl chains in the modified silica has formed. Scanning electron microscope analysis demonstrates dispersion of the uniform-sized modified silica particles.

REFERENCES

1. Li Shuyuan, Qian Jialin, Wang Jianqiu. 27th International Oil Shale Conference summary report // Chinese Journal of Oil Shale. 2007. No. 5. P. 22–27 [in Chinese].
2. Wang Dong-mei, Xu Ying-mei, He De-min, Guan Jun, Zhang Oiu-min. Investigation of mineral composition of oil shale // Asia-Pac. J. Chem. Eng. 2009. Vol. 4, No. 5. P. 691–697.

3. Reinik, J., Heinmaa, J., Mikkola, J.-P., Kordás, K., Kirso, U. Synthesis of calcium-alumino-silicate hydrates from oil shale ash in different alkaline media // *Oil Shale*. 2010. Vol. 27, No. 1. P. 47–57.
4. Reinik, J., Heinmaa, I., Mikkola, J.-P., Kirso, U. Synthesis and characterization of calcium–alumino-silicate hydrates from oil shale ash – Towards industrial applications // *Fuel*. 2008. Vol. 87, No. 10–11. P. 1998–2003.
5. Reinik, J., Heinmaa, I., Mikkola, J.-P., Kirso, U. Hydrothermal alkaline treatment of oil shale ash for synthesis of tobermorites // *Fuel*. 2007. Vol. 86, No. 5–6. P. 669–676.
6. Xu Ying-mei, He De-min, Wang Dong-mei, Lian Yu-huan, Guan Jun, Zhang Qiu-min. Influence of calcination temperature on leaching rate of aluminum and iron impurities in oil shale ash // *Oil Shale*. 2009. Vol. 26, No. 2. P. 163–168.
7. Xu Ying-mei, He De-min, Jiang Hui-ming, Lian Yu-huan, Zhang Wei, Guan Jun, Zhang Qiu-min. Characterization of oil shale processing residues and separated products // *Oil Shale*. 2009. Vol. 26, No. 4. P. 500–512.
8. Feng Zong-yu, Li Yong, Xue Xiang-xin, He Yan, Liu Ping-xian. Preparation of alumina and silica white from oil shale residue // *Mining and Metallurgical Engineering*. 2008. Vol. 28, No. 4. P. 53–57 [in Chinese].
9. Trikkel, A., Kuusik, R., Maljukova, N. Distribution of organic and inorganic ingredients in Estonian oil shale semicoke // *Oil Shale*. 2004. Vol. 21, No. 3. P. 227–236.
10. Wang Qing, Bai Jingru, Sun Baizhong, Sun Jian. Strategy of Huadian oil shale comprehensive utilization // *Oil Shale*. 2005. Vol. 22, No. 3. P. 305–316.
11. You Jun-jun, Ye Song-qing, Liu Zhao-jun, Wang Yun-zhe. Comprehensive development and utilization of oil shale // *Geology of the World*. 2004. Vol. 24, No. 3. P. 251–256 [in Chinese].
12. Arro, H., Prikk, A., Pihu, T., Õpik, I. Utilization of semi-coke of Estonian shale oil industry // *Oil shale*. 2002. Vol. 19, No. 2. P. 117–125.
13. Li Yong, Xue Xiang-xin, Feng Zong-yu. Preparation of precipitated silica from oil shale residue // *Journal of Process Engineering*. 2007. Vol. 7, No. 4. P. 751–754 [in Chinese].
14. Gao Gui-mei, Zou Hai-feng, Gan Shu-cai, Liu Zhao-jun, An Bai-chao, Xu Ji-jing, Li Guang-huan. Preparation and properties of silica nanoparticles from oil shale ash // *Powder Technol.* 2009. Vol. 191, No. 1–2. P. 47–51.
15. Tang Hong-bo, Zhang Xin-meng, Ma Bing-jie, Zhong Yu-hua. Modification technology of nano-silica using hexamethyldisilazane // *Journal of Shenyang University of Technology*. 2007. Vol. 29, No. 6. P. 663–666 [in Chinese].
16. Jesionowski, T., Bula, K., Janiszewski, J., Jurga, J. The influence of filler modification on its aggregation and dispersion behaviour in silica/PBT composite // *Compos. Interface*. 2003. Vol. 10, No. 2–3. P. 225–242 .
17. Yao Ying. Study of the influence about surface active agent to carbonation white carbon // *Tianjin Chemical Industry*. 2006. Vol. 20, No. 4. P. 36–37 [in Chinese].
18. Ouyang Zhao-hui, Wu Lin, Li Kong-biao, Cao Shuchao, Wang Yan. Surface modification of nano-SiO₂ in gas phase // *Chemical Industry and Engineering Progress*. 2005. Vol. 24, No. 11. P. 1265–1268 [in Chinese].
19. Zurawska, J., Krysztafkiewicz, A., Jesionowski, T. Effect of ammonium salts on dispersive and adsorptive parameters of silicas precipitated from sodium metasilicate solution // *Colloid. Surface. A*. 2003. Vol. 223, No. 1–3. P. 201–214.

20. *Yu Xin-wei, Chen Yao*. Surface modification technology of silica // *Journal of Guangzhou University*. 2002. Vol. 1, No 6. P. 12–16 [in Chinese].
21. *Xu Ying-mei, Qi Ji, He De-min, Wang Dong-mei, Chen Hui-ying, Guan Jun, Zhang Qiu-min*. Preparation of amorphous silica from oil shale residue and surface modification by silane coupling agent // *Oil Shale*. 2010. Vol. 27, No. 1. P. 37–46.

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