



Hydrogenation of methyl isobutyl ketone over bifunctional Pt–zeolite catalyst

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ABSTRACT

Methyl isobutyl ketone (MIBK) can be viewed as a key intermediate for the conversion of biomass-derived acetone – the by-product of biobutanol production – to transportation fuel. Zeolite H-ZSM-5 doped with Pt nanoparticles was found to be a highly efficient catalyst for gas-phase hydrogenation of MIBK to methylpentanes with >99% yield at 200 °C. The reaction proceeds via bifunctional metal-acid catalysed pathway involving MIBK hydrogenation to 4-methyl-2-pentanol (MP-ol) on metal sites followed by MP-ol dehydration on acid sites to form olefin and finally olefin hydrogenation to 2-methylpentane (2MP) on metal sites, with all three steps occurring on a single catalyst bed. 2MP thus obtained underwent isomerisation over bifunctional Pt/H-ZSM-5 catalyst to give a mixture of 2- and 3-methylpentanes in a ratio of 83:17. The catalyst did not show any deactivation for at least 16 h on stream.

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1. Introduction

Efficient utilisation of biomass resources is a major goal for academia and industry [1,2]. Presently, about 50% of the crude oil produced worldwide is refined into transportation fuels. The use of biomass-derived fuel such as ethanol and biodiesel can significantly reduce carbon dioxide emission, diversify energy sources and improve energy security. It is expected that biomass-based *n*-butanol (biobutanol) will also play a major role in the next generation of biofuels. Butanol produces more power than ethanol, and 85% butanol/gasoline blends can be used in unmodified petrol engines [3]. Biobutanol can be produced by the acetone–butanol fermentation of carbohydrates and cellulosic raw materials using *Clostridium acetobutylicum* strain that yields butanol together with acetone and ethanol in a weight ratio of 6:3:1 [4,5]. This, however, will produce a surplus of acetone. Therefore, finding new outlets for acetone, preferably in the transportation fuel sector, would improve the economy of biobutanol production. Acetone can be transformed into C₆ and larger organic molecules by aldol condensation. This is employed for industrial production of methyl isobutyl ketone (MIBK), which is used as solvent in paints, coatings and resins. MIBK synthesis (Scheme 1) can be carried out either in three separate steps or more efficiently as one-pot process using a bifunctional metal-acid catalyst, for example, Pd on an acidic support ([6–8] and references therein). MIBK can be viewed as a key intermediate for the conversion of biomass-derived acetone to transportation fuel. MIBK could be deoxygenated by

hydrogenation to 2-methylpentane (2MP) which could be blended with gasoline and used through the existing fuel infrastructure. However, to the best of our knowledge, there is little data available on catalytic hydrogenation of MIBK. Here we report a very efficient gas-phase hydrogenation (hydrodeoxygenation) of MIBK to 2MP via heterogeneous bifunctional metal-acid catalysis using Pt-doped zeolite as the catalyst.

2. Experimental

2.1. Chemicals and materials

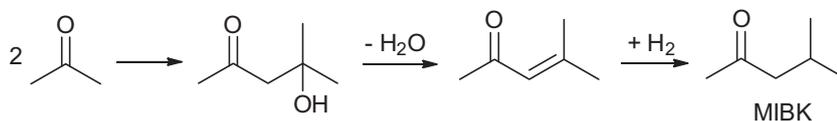
Zeolites H-ZSM-5 (Si/Al = 12, specific surface area $S_{\text{BET}} = 403 \text{ m}^2 \text{ g}^{-1}$), H-Y (Si/Al = 15, $S_{\text{BET}} = 780 \text{ m}^2 \text{ g}^{-1}$) and NH₄-Beta (Si/Al = 12, $S_{\text{BET}} = 680 \text{ m}^2 \text{ g}^{-1}$) were from Zeolyst International. Aerosil 300 silica ($S_{\text{BET}} = 300 \text{ m}^2 \text{ g}^{-1}$) was from Degussa. MIBK (99.0%), copper chromite Cr₂Cu₂O₅ and other chemicals used for catalyst preparation were purchased from Aldrich. Pt and Pd supported on active carbon were from Johnson Matthey. H₂ gas (>99%) was supplied by the British Oxygen Company.

2.2. Techniques

BET surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2010 instrument at –196 °C. Before the measurement, the samples were evacuated at 250 °C for 2 h. Powder X-ray diffraction (XRD) spectra of catalysts were recorded on a PANalytical Xpert diffractometer with a monochromatic Cu K α radiation ($\lambda = 0.154 \text{ nm}$). XRD patterns were attributed using the JCPDS database. ICP-AES

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Scheme 1. MIBK production from acetone.

elemental analysis was carried out on a Spectro Ciros emission spectrometer. Thermo Flash EA 1112 series analyser was used to determine carbon content in spent catalysts. Pt dispersion in catalysts was measured by hydrogen chemisorption on a Micromeritics TPD/TPR 2900 instrument as described previously [7].

2.3. Catalysts preparation

NH₄-Beta was converted to H-Beta by air calcination at 550 °C for 4 h. Pt-doped zeolites were prepared by the literature procedure [9,10] involving adsorption of Pt(II) on to zeolite from 0.01 M aqueous solution of Pt(NH₃)₄(NO₃)₂ followed by washing with distilled water, air calcination at 450 °C for 2 h and reduction by H₂ at 400 °C for 2 h. The Pt loading in zeolite catalysts was determined by ICP analysis. 0.5%Pd/SiO₂ was prepared by wet impregnation of Aerosil 300 with 0.02 M benzene solution of Pd(OAc)₂, followed by drying in a rotary evaporator at 60 °C and reduction with H₂ at 250 °C for 2 h. 0.5%Pt/SiO₂ was prepared by the same procedure using Pt(acac)₂ as a precursor. 5%Cu/SiO₂ was prepared by wet impregnation using an aqueous solution of Cu(NO₃)₂·2.5H₂O, followed by drying in a rotary evaporator, air calcination at 400 °C for 2 h and final reduction with H₂ at 400 °C for 2 h. Copper chromite prior to use was reduced at 400 °C in an H₂ flow for 2 h. After reduction, it exhibited sharp XRD pattern of Cu metal, with (1 1 1) and (2 0 0) reflections at 43.4° and 50.5°, respectively, in agreement with the standard values (JCPDS, copper 04-0836). The catalysts were sieved into a powder of 45–180 μm particle size. Catalyst characterisation is shown in Table 1.

2.4. Catalyst testing

The hydrogenation of MIBK was carried out in the gas phase in flowing H₂. The catalysts were tested at 100–400 °C under atmo-

spheric pressure in a Pyrex fixed-bed down-flow reactor (9 mm internal diameter) fitted with an on-line gas chromatograph (Varian Star 3400 CX instrument with a 30 m × 0.25 mm HP INNOWAX capillary column and a flame ionisation detector). For more accurate analysis of C₁–C₅ hydrocarbon products, a 60 m × 0.32 mm GSGasPro capillary column was used, which allowed for full separation of these hydrocarbons. The temperature in the reactor was controlled by a Eurotherm controller using a thermocouple placed at the top of the catalyst bed. MIBK was fed by passing H₂ flow controlled by a Brooks mass flow controller through a stainless steel saturator, which held liquid MIBK at an appropriate temperature to maintain the chosen reactant concentration. Typically, unless stated otherwise, the saturator temperature was 35 ± 0.3 °C, which gave the MIBK partial pressure of 3.64 kPa (3.6 vol%) [11]. The gas feed entered the reactor at the top at a flow rate of 20 ml min⁻¹. The downstream gas lines and valves were heated to 180 °C to prevent substrate and product condensation. Unless otherwise indicated, the catalyst bed contained 0.2 g of powdered catalyst (45–180 μm particle size). In some cases, a smaller amount of catalyst diluted with silica to 0.2 g was used to reduce conversion. Prior to reaction, the catalysts were pre-treated in H₂ flow for 1 h at the reaction temperature. Once reaction started, the downstream gas flow was analysed by the on-line GC to obtain MIBK conversion and product selectivity. The selectivity was defined as moles of product formed per one mole of MIBK converted and quoted in mole per cent.

3. Results and discussion

First, we tested a number of conventional supported metal catalysts comprising Pd, Pt and Cu supported on silica and active carbon for MIBK hydrogenation in the temperature range of 100–400 °C. At 100–200 °C, these catalysts were active for the hydrogenation of MIBK to 4-methyl-2-pentanol (MP-ol) (Table 2). The selectivity to MP-ol decreased with increasing temperature due to formation of 2MP and hydrogenolysis of C–C bonds giving C₁–C₅ hydrocarbons. The highest 2MP selectivities, 87–94%, were observed for 10%Pt/C and 10%Pd/C catalysts at 52–84% conversion at a temperature as high as 300 °C (Table 2), which indicates the difficulty of direct hydrogenation of MP-ol to 2MP.

Table 1
Catalyst characterisation.

Catalyst ^a	Si/ Al ^b	S _{BET} ^c (m ² g ⁻¹)	Pore volume ^d (cm ³ g ⁻¹)	Pore diameter ^e (Å)	D ^f
0.30%Pt/H-ZSM-5	12	362	0.23	25	0.88
0.06%Pt/H-ZSM-5	12	357	0.22	25	0.87
0.39%Pt/H-Beta	12	491	0.61	50	0.72
0.45%Pt/H-Y	15	690	0.44	26	0.62
5%Cu/SiO ₂ ^g		251	0.74	118	
0.5%Pd/SiO ₂ ^g		255	0.68	106	0.62
0.5%Pt/SiO ₂ ^g		287	0.52	74	0.27
10%Pt/C ^h		801	0.58	29	
5%Pd/C ^h		924	0.58	25	
10%Pd/C ^h		823	0.57	28	
Cr ₂ Cu ₂ O ₅ ⁱ		55	0.13	93	

^a Pt loading (wt%) from ICP analysis unless stated otherwise.

^b Si/Al atomic ratio in zeolites.

^c BET surface area.

^d Single point total pore volume.

^e Average BET pore diameter.

^f Metal dispersion in fresh catalysts from H₂ chemisorption.

^g Metal loading from preparation stoichiometry.

^h Metal loading from supplier.

ⁱ After reduction at 400 °C in H₂ for 2 h.

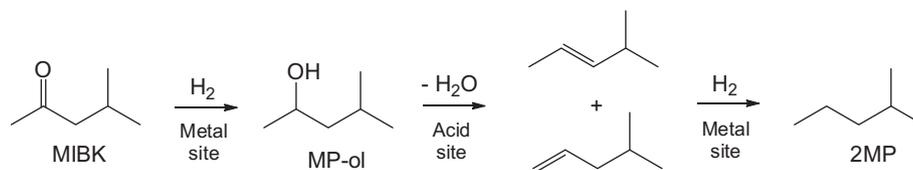
Table 2
Hydrogenation of MIBK on supported metal catalysts.^a

Catalyst	Conversion (%)	Selectivity (%)		
		2MP	MP-ol	Other
0.5%Pt/SiO ₂	46	47	53	0
10%Pt/C	47	40	56	4
10%Pt/C ^b	52	87	9	4
0.5%Pd/SiO ₂	46	0	47	53
10%Pd/C	37	28	66	6
10%Pd/C ^b	84	94	5	1
5%Cu/SiO ₂	34	0	100	0
2CuO·Cr ₂ O ₃ ^c	41	0	82	18

^a At 200 °C, 0.20 g catalyst pre-treated in H₂ at reaction temperature for 1 h, 3.6% MIBK in H₂ flow, 20 ml min⁻¹ flow rate, 4 h time on stream.

^b At 300 °C.

^c Pre-reduced in H₂ at 400 °C for 2 h.



Scheme 2. Hydrogenation of MIBK via bifunctional metal-acid catalysis.

Table 3
Hydrogenation of MIBK over bifunctional Pt/zeolite catalysts.^a

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)			
			2MP	3MP	MP-ol	Other
H-ZSM-5	100	0	0	0	0	0
H-ZSM-5	200	20	9	0	7	84 ^b
0.30%Pt/H-ZSM-5	100	94	65	0	34	1
0.30%Pt/H-ZSM-5	200	100	83	17	0	0
0.39%Pt/H-Beta	100	92	58	0	38	4
0.39%Pt/H-Beta	200	44	70	4	0	26 ^c
0.45%Pt/H-Y	100	98	36	0	49	15
0.45%Pt/H-Y	200	81	55	2	0	43 ^c

^a 0.20 g catalyst pre-treated in H₂ at reaction temperature for 1 h, 3.6% MIBK in H₂ flow, 20 ml min⁻¹ flow rate, 4 h time on stream.

^b C₁–C₅ cracking products, mainly propene and butenes, together with small amount of C₆₊ condensation products.

^c Mainly C₆₊ condensation products.

Next we attempted to explore bifunctional metal-acid catalysed pathway to achieve MIBK-to-2MP hydrogenation in one step on a single catalyst bed using platinum metals supported on zeolites as the bifunctional catalysts. This pathway would involve MIBK hydrogenation to MP-ol on metal sites followed by MP-ol dehydration on acid sites to form olefin and finally olefin hydrogenation to 2MP on metal sites (Scheme 2). Since dehydration of secondary alcohols on acid catalysts is fast [12,13] and so is hydrogenation of C=C bond on platinum metals, the bifunctional pathway was expected to be more efficient than the hydrogenation only pathway. Our study proved that this was indeed the case for Pt/zeolite catalysts.

Representative results are shown in Table 3, with zeolite catalysts placed in the order of increasing their pore size. The zeolites used, H-ZSM-5, H-Beta and H-Y, had close Si/Al atomic ratios (Si/Al = 12–15) and hence comparable proton site densities. Their acid strength decreases in the order H-ZSM-5 > H-Beta > H-Y [14,15]. The Pt/zeolite catalysts had high crystallinity and exhibited standard XRD patterns of the corresponding zeolites. No Pt reflections were observed in XRD spectra of these catalysts, indicating fine dispersion of Pt metal, as also confirmed by H₂ adsorption (Table 1). Despite Pt doping was carried out similarly for all zeolites, using the same 0.01 M aqueous solution of Pt(NH₃)₄(NO₃)₂, the final Pt loading varied between 0.30 and 0.45 wt%, increasing with the pore diameter of zeolite. This indicates that Pt loading was controlled by the zeolite pore size.

In a blank run, H-ZSM-5 itself was not active at all at 100 °C. At 200 °C, it converted 20% of MIBK to give mainly C₁–C₅ cracking products, mostly propene and butenes, together with small amounts of 2MP and MP-ol. Doping of zeolites with Pt greatly increased catalyst activity already at 100 °C, giving 92–98% MIBK conversion to a mixture of 2MP and MP-ol in a molar ratio of 1:(0.5–1.4). At this temperature, the dehydration of MP-ol was not complete, and the MP-ol/2MP ratio decreased with increasing zeolite acid strength: 1.36 (H-Y) > 0.66 (H-Beta) > 0.52 (H-ZSM-5), which can be explained by acceleration of alcohol dehydration with increasing catalyst acid strength. It should be noted that no 2MP isomerisation was observed at 100 °C. Increasing the temperature to 200 °C led to complete dehydration of MP-ol, giving 2MP

as the main product with 55–83 selectivity. At 200 °C, 2MP isomerised to form 3-methylpentane (3MP) and traces of *n*-hexane, in agreement with the literature [16]. As expected, the isomerisation correlates with zeolite acid strength as indicated by 3MP/2MP product ratio: 0.20 (Pt/H-ZSM-5) > 0.057 (Pt/H-Beta) > 0.036 (Pt/H-Y) (Table 3). The mechanism of alkane isomerisation over bifunctional catalysts has been discussed elsewhere ([16] and references therein). It involves alkane dehydrogenation on Pt to form an alkene followed by alkene skeletal isomerisation on acid sites and finally alkene hydrogenation on Pt to yield the corresponding alkane isomer. In our case, 4-methylpentene-1 and 4-methylpentene-2 formed in MP-ol dehydration (Scheme 2) may isomerise on zeolite acid sites to give eventually 3MP. The total selectivity to methylpentanes increases in the order: Pt/H-Y (57%) < Pt/H-Beta (74%) < Pt/H-ZSM-5 (>99%). Therefore, amongst the Pt/zeolite catalysts studied, Pt/H-ZSM-5 clearly stands out giving >99% selectivity to methylpentanes at 100% MIBK conversion at 200 °C (Table 3). Other catalysts, Pt/H-Beta and Pt/H-Y, gave significant amounts of unidentified C₆₊ condensation by-products. These can be attributed to aldol condensation of MIBK. The amount of bulky C₆₊ by-products formed increased with the pore size of zeolites:

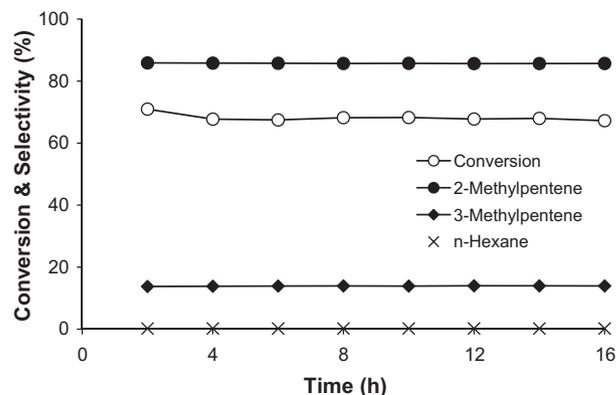


Fig. 1. Time course for MIBK hydrogenation over 0.3%Pt/H-ZSM-5 (0.05 g) diluted with 0.15 g SiO₂ at 200 °C, 3.6% MIBK, 20 ml min⁻¹ H₂ flow rate.

Table 4
Effect of MIBK concentration.^a

[MIBK] (vol.%)	3.6	4.9	6.4
Rate (mol h ⁻¹ g ⁻¹)	0.0038	0.0037	0.0036

^a 0.06%Pt/H-ZSM-5 (0.05 g) diluted with 0.15 g SiO₂, 200 °C, 20 ml min⁻¹ H₂ flow rate, 5 h time on stream. The rates were measured at 6–10% MIBK conversion.

Table 5
Effect of Pt loading.^a

Catalyst	Pt dispersion	Conversion (%)	Selectivity (%)			
			2MP	3MP	n-Hexane	Other
0.06%Pt/H-ZSM-5	0.87	11	75	15	2	8
0.3%Pt/H-ZSM-5	0.88	67	86	14	<1	<1

^a 0.05 g catalyst diluted with 0.15 g SiO₂, 200 °C, 3.6% MIBK, 20 ml min⁻¹ H₂ flow rate, 6 h time on stream.

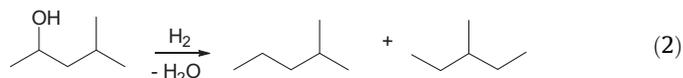
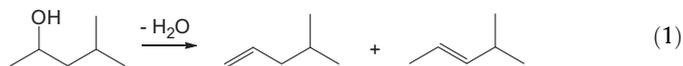
H-ZSM-5 (5.5 Å) < H-Beta (7.6 × 6.4 Å) < H-Y (7.5 Å), which is an indication of “shape-selective” catalysis. The amount of coke (C wt%) found in spent catalysts after reaction (200 °C, 6 h) also increased in this order: 5.9 (H-ZSM-5) < 10.5 (H-Beta) < 11.9 (H-Y). This is probably the reason for the drop in conversion at 200 °C for the larger pore zeolites H-Beta and H-Y (Table 3).

The Pt/H-ZSM-5 catalyst showed excellent performance stability. It reached steady state in about 2 h and operated without deactivation for at least 16 h (Fig. 1). It should be noted that in this run to set the conversion at about 70%, the amount of catalyst had to be reduced 4-fold compared to that in Table 3.

The rate of reaction over Pt/H-ZSM-5 catalyst practically did not change with MIBK concentration in the gas feed (Table 4), indicating that the order in MIBK is close to zero. Therefore, in this system, MIBK conversion is directly proportional to the reaction rate. The reaction had a rather low activation energy of 18 kJ/mol, as determined for 0.06%Pt/H-ZSM-5 catalyst in the temperature range of 185–230 °C. This implies that the reaction may be controlled by internal diffusion in zeolite micropores. MIBK conversion was found to increase from 11% to 67% with increasing Pt loading from 0.06% to 0.30% (Table 5), that is, scaled almost proportionally with the Pt loading. Given the Pt dispersion was about the same for these loadings (Table 1), this means that the reaction order in Pt is close to one. From these results, the apparent turnover frequency (TOF) was estimated to be 1200 h⁻¹ per exposed Pt atom at 200 °C. This value, however, may be restricted by diffusion limitations. Importantly, the selectivity to 2MP and 3MP practically did not change with Pt loading (Table 5) and MIBK conversion (cf. entry 4 in Table 3 with entry 2 in Table 5). This suggests that hydrogenation of MIBK to MP-ol on Pt sites is the slowest step in Scheme 2; subsequent dehydration and hydrogenation steps appear to be fast under the chosen conditions at 200 °C.

Further, to prove the bifunctional mechanism (Scheme 2), we tested the dehydration of MP-ol over 0.3%Pt/H-ZSM-5 at 200 °C

under the conditions applied for MIBK hydrogenation (Table 3), except for using N₂ (20 ml min⁻¹) instead of H₂. As expected, the reaction was very fast, yielding two olefins, 4-methylpentene-1 and 4-methylpentene-2, at 100% conversion (Eq. (1)). The same reaction under H₂ instead of N₂ gave an 85:15 mixture of 2- and 3-methylpentanes in a 100% yield (Eq. (2)). These results, therefore, support the bifunctional mechanism for MIBK hydrogenation over Pt/H-ZSM-5 catalyst.



4. Conclusions

MIBK may be viewed as a key intermediate for the conversion of biomass-derived acetone to transportation fuel. Produced by one-step (one-pot) hydrocondensation of acetone [6–8], MIBK can be further efficiently hydrogenated *via* metal-acid bifunctional pathway on a single bed containing Pt/H-ZSM-5 catalyst to give methylpentanes with >99% yield. The methylpentenes thus obtained could be blended with gasoline and used through the existing fuel infrastructure.

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References

- [1] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 107 (2007) 2411–2502.
- [2] E.L. Kunkes, D.A. Simonetti, R.M. West, J.C. Serrano-Ruiz, C.A. Gaertner, J.A. Dumesic, *Science* 322 (2008) 417–421.
- [3] P. Durre, *Ann. N. Y. Acad. Sci.* 1125 (2008) 353–362.
- [4] D.T. Jones, D.R. Woods, *Microbiol. Rev.* 50 (1986) 484–524.
- [5] V.V. Zverlov, O. Berezina, G.A. Velikodvorskaya, W.H. Schwarz, *Appl. Microbiol. Biotechnol.* 71 (2006) 587–597.
- [6] R.D. Hetterley, E.F. Kozhevnikova, I.V. Kozhevnikov, *Chem. Commun.* (2006) 782–784.
- [7] F. Al-Wadaani, E.F. Kozhevnikova, I.V. Kozhevnikov, *J. Catal.* 257 (2008) 199–205.
- [8] R.D. Hetterley, R. Mackey, J.T.A. Jones, Y.Z. Khimyak, A.M. Fogg, I.V. Kozhevnikov, *J. Catal.* 258 (2008) 250–255.
- [9] A.C.M. van den Broek, J. van Grondelle, R.A. van Santen, *J. Catal.* 167 (1997) 417–424.
- [10] J. de Graaf, A.J. van Dillen, K.P. de Jong, D.C. Koningsberger, *J. Catal.* 203 (2001) 307–321.
- [11] CRC, *Handbook of Chemistry and Physics*, 88th ed., 2007–2008.
- [12] J. Macht, M. Janik, M. Neurock, E. Iglesia, *J. Am. Chem. Soc.* 130 (2008) 10369–10379.
- [13] A.M. Alsalmé, P.V. Wiper, Y.Z. Khimyak, E.F. Kozhevnikova, I.V. Kozhevnikov, *J. Catal.* 276 (2010) 181–189.
- [14] M. Brandle, J. Sauer, *J. Am. Chem. Soc.* 120 (1998) 1556–1570.
- [15] S.G. Hegde, R. Kumar, R.N. Bhat, P. Ratnasamy, *Zeolites* 9 (1989) 231–237.
- [16] J. Macht, R.T. Carr, E. Iglesia, *J. Catal.* 264 (2009) 54–66.